2019 – Hydrogen Fuel R&D
Summary of Annual Merit Review of the Hydrogen Fuel R&D Subprogram

The Hydrogen Fuel R&D subprogram focuses on early-stage research and development (R&D) to reduce the cost and improve the reliability of technologies used to produce and store hydrogen from diverse domestic energy resources. The subprogram is divided into two categories: (1) Hydrogen Production R&D and (2) Hydrogen Storage R&D. Efforts in each area leverage expertise and capabilities at the national laboratories and encourage collaboration witth industry through the Hydrogen Materials–Advanced Research Consortium (HyMARC) and the HydroGEN consortium. Both consortia are part of the U.S. Department of Energy's (DOE's) Energy Materials Network (EMN). The subprogram also covers early-stage R&D in materials for hydrogen production and storage; this work is specifically targeted to support the H2@Scale initiative.

In fiscal year (FY) 2019, production projects focused primarily on early-stage R&D for advanced water-splitting materials and systems funded through HydroGEN. Production pathways under investigation included advanced high- and low-temperature electrochemical water splitting and direct solar thermochemical (STCH) and photoelectrochemical (PEC) water splitting. Hydrogen storage projects in FY 2019 focused on materials-based hydrogen storage R&D through HyMARC, including the discovery, design, synthesis, and validation of metal–organic frameworks (MOFs), metal hydrides, and other innovative concepts with the potential to reach high energy densities as well as favorable kinetics and thermodynamics. A new effort on hydrogen carriers (also under HyMARC) started in FY 2019 to address challenges associated with transporting and storing large quantities of hydrogen and to enable progress toward achieving the H2@Scale vision. The subprogram continued early-stage R&D for onboard high-pressure storage through the development of precursor fibers for low-cost, high-strength carbon fiber. All projects under the Hydrogen Fuel R&D subprogram continued to be evaluated with respect to their potential to meet DOE's cost and performance targets for the near and long terms.

Summary of Hydrogen Fuel R&D Subprogram and Reviewer Comments

Reviewers of the Hydrogen Production R&D category commented that the projects were focused on achieving DOE cost and performance targets across the various technology pathways. The reviewers responded favorably to the approach of these early-stage R&D efforts, mentioning that they were logical and show high probability of impact. Projects were also commended for their combination of experimental and computational methods in their approach to advancing fundamental understanding of underlying concepts, as well as meeting project targets. The advanced water-splitting projects were praised for their strong interaction with the national laboratories and successful leveraging of capabilities through the HydroGEN consortium. Projects were also commended for their contributions of resources to the HydroGEN Data Hub. Reviewers commented that they would like to see increased attention to accurate cost models as these projects move into the next phase.

Within the Hydrogen Storage R&D category portfolio, reviewers highlighted the continued synergy of resources, priorities, and technical goals. The reviewers are encouraged that closer integration of early-stage production and storage R&D efforts will lead to successful overlap with infrastructure activities to maximize R&D impact and increase the likelihood of success for the overall Hydrogen and Fuel Cells Program (the Program). Reviewers praised the subprogram category's world-class team members, productive collaborations, project management, and open communication with stakeholders. The reviewers commended the Program's consistent engagement and flexibility to meet industry needs. HyMARC continued to be highly regarded as the nucleus to influence foundational scientific understanding and world-class resources and facilities across multiple institutions. The consolidation of the HyMARC and Hydrogen Storage Characterization Optimization Research Effort (HySCORE) teams has broadened the scope and provided a more streamlined way to address R&D with limited overlap and duplication among the seedling projects. While the material-based hydrogen storage work was generally commended, reviewers did note a desire for additional work and portfolio balance with more traditional high-pressure storage tanks.

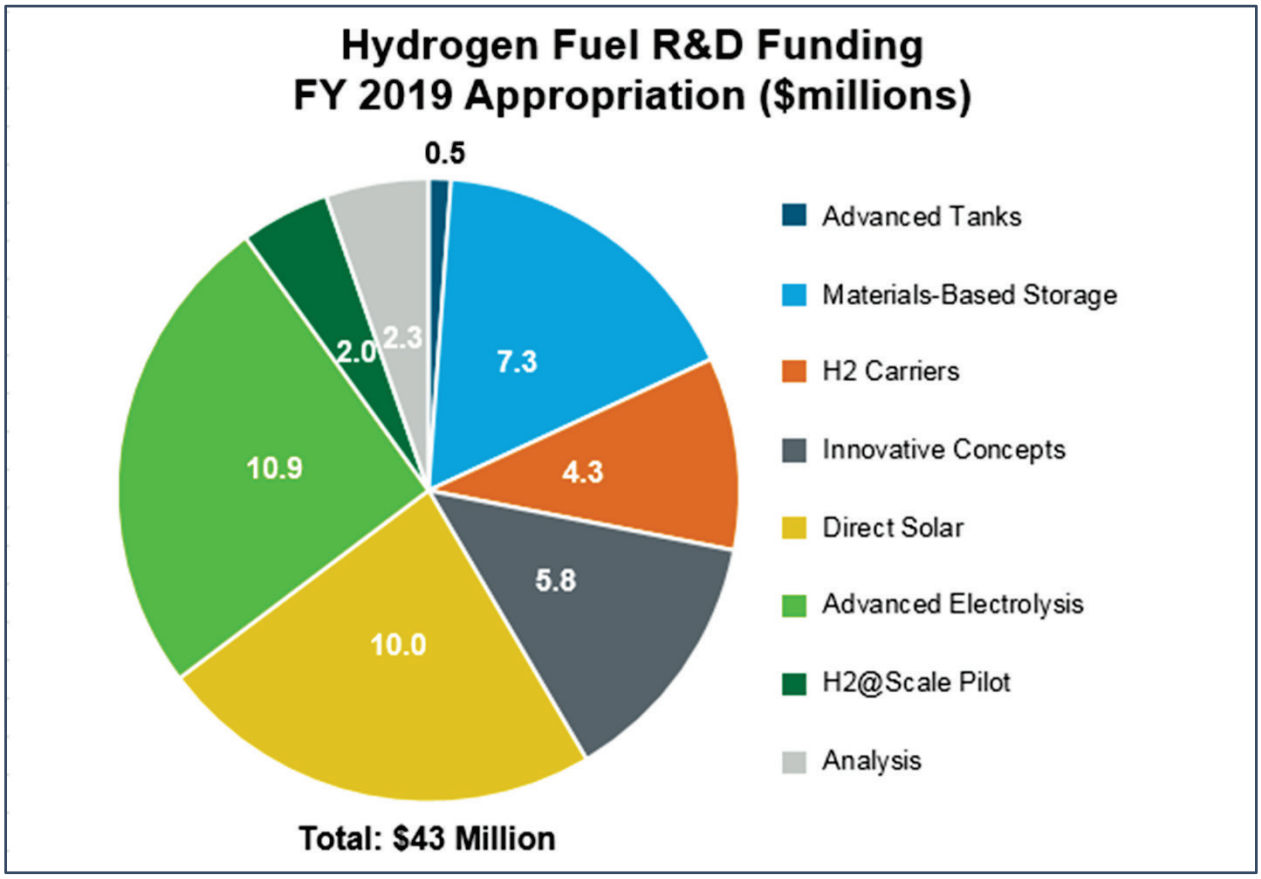
Twenty-five hydrogen production projects were reviewed, with overall favorable scores ranging from 2.9 to 3.7, with 3.4 as the average score. The Hydrogen Storage R&D portfolio was represented by fourteen oral presentations and eight posters (including one Small Business Innovation Research project) in FY 2019. Out of the fourteen

projects reviewed, nine focused on materials development, two on analysis, and one on engineering. In general, the reviewers' scores for the projects were good, with scores of 3.6, 3.1, and 3.3 for the highest, lowest, and average scores, respectively.

Each of the individual project reports in this section contains a project summary, the project's overall score and average scores for each question, and the project-level reviewer comments.

Hydrogen Fuel R&D Funding

The FY 2019 appropriation for the Hydrogen Fuel R&D subprogram totaled $39 million, with an additional $4 million from the Hydrogen Infrastructure R&D appropriations to support the hydrogen carrier development activities. Of these appropriations, $30 million was allocated for hydrogen production research and $13 million for hydrogen storage research, as shown in the figure below. Projects funded in the Hydrogen Production R&D portfolio are expected to accelerate materials development for advanced water-splitting technologies toward meeting DOE targets, and this emphasis is expected to continue into FY 2020.



* Note: FY 2019 funding includes $4 million from Hydrogen Infrastructure R&D to support hydrogen carrier R&D

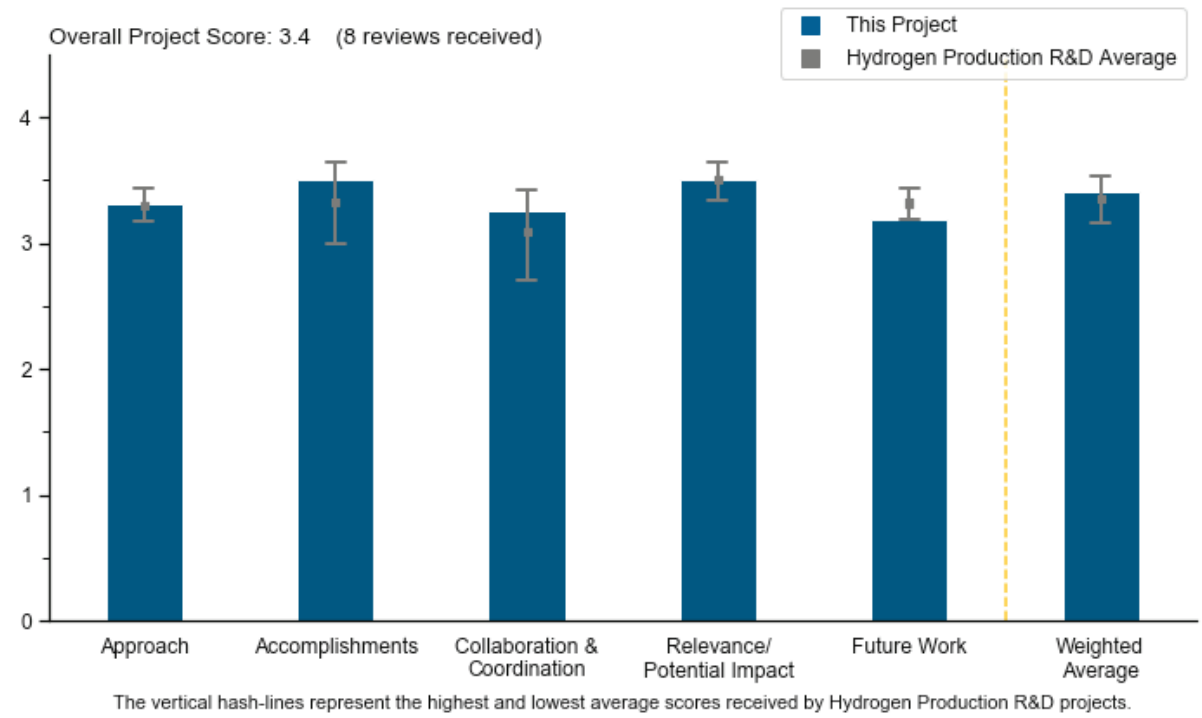
Project #P-102: Analysis of Advanced Hydrogen Production Pathways

Brian James, Strategic Analysis, Inc.

Brief Summary of Project

This project investigates high-priority hydrogen production and delivery pathways selected or suggested by the U.S. Department of Energy (DOE), and subsequently analyzes them with respect to economic and technical drivers. The project provides complete hydrogen production and delivery pathway definition, performance, and economic analysis not elsewhere available. The current effort is updating the Hydrogen Analysis (H2A) model cases for polymer electrolyte membrane (PEM) and solid oxide electrolysis with updated performance and cost data. The project addresses several DOE-identified barriers related to transmission methods for energy carriers and hydrogen generation by water electrolysis. The prime (Strategic Analysis, Inc. [SA]) is collaborating with project partners National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), electrolyzer companies, and other technology experts to model state-of-the-art (SOA) and future systems (e.g., photoelectrochemical [PEC] hydrogen production and solar thermochemical hydrogen [STCH] production).

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.3** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approaches used for the hydrogen production and the energy transmission analyses are sound. The attempt to obtain performance and cost data from six electrolyzer companies and research groups is excellent. Similarly, the approach to the analysis of energy transmission methods is sound and informative. In particular, comparison of total cost of transmission using multiple metrics (i.e., dollars per mile, dollars per megawatt-mile, and dollars per megawatt-hour) provides level comparisons and meaningful insight.
- The approach is based on industry surveys followed by in-depth technoeconomic analysis (TEA). The methods used for PEM electrolysis and energy transmission are appropriate. Particularly noteworthy is the modification of the energy transmission cost parameter from cost per mile to cost per megawatt-hour per

mile. This metric shows a significant difference in the performance of the energy transport technologies. The solid oxide electrolysis work is in its infancy but is likely to succeed if it follows the protocols outlined for PEM.

- The bottom-up cost-modeling approach taken by SA provides the community with critical insights into technology pinch points and scale-up challenges to tackle.
- The project is very diverse, ranging from an in-depth summary of electrolysis accounting and cost to a comparison of energy transfer and infrastructure costs for gas and liquid pipelines versus high-voltage transmission lines. The project uses a quantitative approach wherein all assumptions are explicitly spelled out. Any cost study will be a continuously moving target as compared to a more physics-based approach founded on materials, energy consumption, and book-end efficiencies.
- The analysis of several of the barriers associated with hydrogen generation via electrolysis is interesting and insightful, as is the comparison of hydrogen as an energy-carrying medium with other fuel options. The investigators' presentation choices for hydrogen generation analysis results are sometimes difficult to understand. For example, the team distributes capital cost information for mechanical balance of plant (BOP) over the amount of hydrogen produced per day; however, information is not provided indicating the period of time for which this cost rate is anticipated (i.e., the period of time over which these costs are spread before replacement costs will be incurred). Similarly, lifetimes of electrical BOP components are not mentioned. The investigators also mention that their analyses should address system efficiency and manufacturing; however, their analysis for PEM electrolysis does not appear to contain explicit metrics associated with these barriers. The degree to which these barriers affect the investigators' work is unclear. The presentation method for the analysis of energy transmission was more coherent and well thought out. However, the small number of references on which the team bases the analysis is concerning. Only a few pipeline cost models are cited. On the other hand, the small number of references may only underscore the need for more rigorous analysis and model validation and development within the community.
- The project does not take spikes, off time, lower capacity factors, or scaling for peak and non-peak types and multiple stacks into account. The results of other studies such as Lawrence Berkeley National Laboratory's report, *A Total Cost of Ownership Model for Solid Oxide Fuel Cells in Combined Heat and Power and Power-Only Applications*, should be considered, as it is possible that their results may translate to electrolysis. Transmission work should inform other parts of the DOE Hydrogen and Fuel Cells Program (the Program). Furthermore, transmission work should consider carriers and non-pipeline transmission of hydrogen including trucking in both high-pressure and liquid states.
- As with any analysis conducted at any level of fidelity, the inputs and assumptions in this analysis have a significant and indelible imprint on the result. SA's work flow and analytical results carry caveats warning of sparse information throughout their approach. Nonetheless, the investigators decided to conduct the analysis. The investigators should communicate the effect sparse information has on the result to inspire more confidence in the result.
- Some assumptions were clearly "cherry-picked," to the detriment of competing technologies. For example, it seems disingenuous to assume combustion for a natural gas re-electrification pathway achieves 33% efficiency and assume a fuel cell achieves 50% efficiency in the hydrogen case.

Question 2: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- These unbiased updates to the electrolysis cases are extremely valuable to the hydrogen community. SA's efforts to thoughtfully improve the modeling approach to increase the robustness of the results should be applauded. Modeling dollars per square centimeter versus dollars per kilowatt for electrolyzers is an example of one such improvement. The electrolyzer updates, especially the long-distance energy transmission cost analysis, should be published in a DOE record as soon as possible. The energy transmission work should also be published in the peer-reviewed open literature as soon as possible. The publication of this work will have a large influence on discussions around investing in electricity versus hydrogen infrastructure, which are taking place globally.
- Approach and assumptions aside, the progress made by the investigators has been excellent. Their results on hydrogen production cost using PEM electrolysis provide insight into the primary cost drivers and the

degree to which these drivers may override cost reduction potential in future systems. It should be noted that several offsets are present that limit, and indeed eliminate, the possibility of cost reduction in future systems. Rather than directly commenting on this elimination, these results may indicate how aspects of the investigators' methodology have limiting assumptions, for example, the degree to which the investigators do or do not assess future technology to be less costly than current technology. Although not presented directly here, the analysis may show where breakthrough innovations must happen in order for hydrogen production cost to meet, if not exceed, DOE targets. Likewise, progress on energy transmission analysis and the conclusions drawn so far offer fascinating insight into the costliness of electricity transmission and the potential for hydrogen and other fuels to dramatically lower this portion of overall cost.

- SA was able to generate a great deal of work, given the limited budget. The effort involved in gathering information and forging an analytical result from it is appreciable.
- The investigators have made good progress toward project goals. Many milestones were achieved several months in advance. The April 2019 milestone is not shown to be completed, but this is likely a result of the Program Annual Merit Review occurring one month after presentations are submitted.
- Significant progress has been made, particularly in terms of PEM and transmission analysis. The analysis reports its findings in ways that are highly quantitative and seemingly transferable. One area that could be improved is the rate of industrial survey response, though this improvement is likely difficult to achieve.
- It is unclear why the investigators believe dollars per square centimeter to be a better cost metric. On slide 7, a desire "to decouple cost from performance" is expressed. Clarification on the benefits of decoupling cost from performance may suffice to answer this question. The Current Central case requires four ~25 MW systems, and the Future Central case relies on two 50 MW systems—perhaps these assumptions are based on the survey. Only Giner ELX has mentioned a (very) large 5 MW stack, so a 25 MW stack seems impressive.
- The results from the electrolysis (i.e., the hydrogen production via water splitting) portion of the study appear modest and incremental. Although the team successfully reached out to six electrolyzer manufacturers for data collection, the data quality and response rate are unclear. For that matter, it is unclear how many manufacturers are in favor of PEM versus solid oxide electrolyzers. The project team reports "general agreement" on current density and voltage data. However, it would be beneficial to quantify the sample representativeness of the blinded respondents' responses, perhaps in the form of standard deviation or uncertainty ranges. Similarly, the project team indicated they obtained limited data on cost. It would be helpful to specify a measure of reliability of the cost-related data. Slide 10 indicates that the study results for future stack costs appear to be more reliable than the current case. These results may signal that the uncertainty assumptions should be revisited.
- It is unclear whether the electrolysis accounts for capacity factors. Furthermore, it is unclear whether costs are consistent with the current SOA, especially when combined with delivery that is much higher than that projected.

Question 3: Collaboration and coordination

This project was rated **3.3** for its engagement with and coordination of project partners and interaction with other entities.

- The project team forged good connections with NREL and ANL. It is great to see that industrial collaborators, though unnamed, are contributing information to the analysis and participating in the review process. It would be interesting to discuss the industry view of the methods and results. It would also be helpful to understand whether the industry finds this level of information useful or would be likely to develop a business case from these results.
- The team has shown good integration with partners, particularly NREL, for project modeling and validation.
- The collaboration and data collection from the electrolyzer manufacturers and outside research groups appear to be valuable. Although the blinding of manufacturer names is understandable, it is unclear why the research groups were not named.
- As the technologies being investigated by SA mature, it is naturally becoming more difficult to obtain survey responses high in quality and quantity. DOE may have a role to play in facilitating the acquisition of what may be considered confidential information in a way that ensures complete anonymity and precludes

damage to the provider. In other words, SA requires DOE's assistance in order to achieve very high collaboration ratings.

- The project received good input from DOE and from other national laboratories. Unfortunately, the missing electrolysis input and the literature-focused comparison of infrastructure and pipeline costs indicate that industry was not extremely integrated in the project. Given the breadth of the technology review, the preference to focus on literature comparisons is understandable.
- The project team collaborated well but may not have obtained enough industrial feedback. The role of the national laboratories is unclear, and it seems there may be overlap, as many laboratories have strong TEA, life-cycle analysis (LCA), and total cost of ownership (TCO) scientists.
- The investigators acknowledge their collaborators and are somewhat clear on the contributions these individuals make to the overall effort. The presentation slides use somewhat ambiguous language regarding collaborator contributions (e.g., "assisted with model runs," "vetted process work"). Clarifying these contributions in future reviews is recommended.
- The team is strong. However, the PEM electrolyzer questionnaire sent in December of 2018 seems far too detailed. With over 40 questionnaire parameters ranging from catalyst loading to operation and maintenance (O&M) costs, more than half of which are labeled "critical," it is not surprising that the project team received such a limited number of responses.

Question 4: Relevance/potential impact

This project was rated **3.5** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This impact of this project lies in its reevaluation of H2A models. This reevaluation is necessary to ensure that the model used for evaluating systems is valid and current.
- SA TEAs such as the ones presented here are a gold standard used by industry to understand key hydrogen technologies.
- The relevance of the hydrogen production cost update portion of the study is straightforward and needed, especially considering the ongoing reduction of renewable electricity price and increased shipments in PEM units. However, the relevance and potential impact of the energy transmission analysis portion of the project is very strong. The results are significant and novel in that they challenge the commonly accepted notion that electrical grid is the preferred means of renewable energy transmission to consumers.
- The periodic cost updates for electrolysis, along with information on fossil fuel energy transmission, are very relevant to keeping DOE research programs on track. The cost analysis helped demonstrate changes in raw materials and capital costs between the 2019 and 2013 studies. Since simple scaling was used, it is not clear that the project will have a large impact on how existing projects are managed or evaluated.
- This project offers important contributions to stakeholders and may also be important for designing targets.
- The investigators provide information useful to the Fuel Cell Technologies Office (FCTO) and the entire hydrogen fuel cell community. The impact of this project is somewhat limited by its lack of certain types of information and by the presence of several unstated assumptions. It would be useful to provide these details in the reports produced and delivered to DOE and later share these details with the larger community. The impact of the analyses performed could be made even stronger by tying the results to conclusions about ways in which technology needs to change (in performance or cost) to reach DOE targets. This is perhaps outside of the scope of the project but would add tremendous value and reduce the need for such analysis by others at a later date.
- It would be more helpful to show today's actual capital costs converted to dollars per kilogram. Large (by today's standards) projects in the 5–10 MW range for energy storage are in development; therefore, it would be nice to have this data more readily available. It will be many years before "Current Cases" for hydrogen production are anywhere near $5/kg (as stated on slide 14), and this production value is very near the value assumed for "Future Cases." A "current" case should be achievable within roughly a year.
- The notion that electricity cost makes the largest contribution to the ultimate hydrogen cost for PEM electrolysis is not news, and revisiting this case study is not useful. It would perhaps be more useful to dedicate resources elsewhere. The energy transmission study is very intriguing, and the result is counter-intuitive for a lay person. Order-of-magnitude differences in cost for carrying energy via electricity

transmission versus other fuel types are notable and have the potential to influence a range of issues that concern policy makers and industrialists.

Question 5: Proposed future work

This project was rated **3.2** for effective and logical planning.

- The future work builds on the progress made so far. It is specific, relevant, and well planned. This project is on track to update the H2A for relevant hydrogen technologies and serve as a good comparison for energy transmission costs, which are important when considering a nationwide energy grid.
- The future sensitivity analysis on the PEM electrolysis and the future exploration of industry feedback will be very interesting and helpful, considering the scale and increased number of projects in North America and around the world. Solid oxide electrolyzers still appear to be an out-year technology in the long term, similar to PEC objectives. The primary value is breaking down silos across FCTO subareas and ensuring that different areas are using a similar basis for reports and technology prioritizations (i.e., delivery, analysis, and target-setting coordination).
- Solid oxide electrolysis is a very good target for an updated analysis.
- The stated future work for the PEM and solid oxide analysis looks good, especially the error and sensitivity analyses. It is suggested that the team carry out a simple data quality or representativeness analysis on the collected industry data. On the other hand, there is no meaningful operational or demonstration data for PEC- or STCH-based hydrogen production technologies to justify similarly detailed cost analyses at this time. Instead, it is strongly recommended that the project team publish the energy transmission results in a peer-reviewed journal. The results are significant and impactful enough to necessitate a wide distribution beyond the internal DOE report. Furthermore, the project team should consider future work that includes the cost of a combination of various energy production and transmission pathways.
- Many of the future activities for analysis of hydrogen generation technologies mentioned in this project (e.g., sensitivity and error analyses, non-electrolysis methods) are important, and the plan for their inclusion is appreciated. Perhaps a similar suite of activities should be developed for the transmission analyses. Additionally, the project may benefit from exploring ways in which the information can best be used by the energy community.
- Transmission should be expanded to other possibilities. For solid oxide and PEM fuel cells, there has already been Design for Manufacture and Assembly work done. Therefore, it is necessary to determine key differences for electrolysis and leverage those differences.
- More work on PEM H2A analysis seems redundant. Also, both PEC and STCH water-splitting technologies are at very low technology readiness levels. One might suggest postponing these studies until sufficient data emerges to provide a robust outcome to the analysis. Otherwise, predictions for these technology pathways to attain commercial viability, or even meet DOE cost targets, are not believable.
- The "cherry-picking" should be reduced, and actual current cases ($15/kg H_2) should be shown. This would be more helpful for audience members who work with utilities to develop large-scale energy storage projects.

Project strengths:

- Availability of empirical or manufacturer data provides a strong foundation for the electolyzer portion of the project. However, the energy transmission study is undoubtedly the highlight of the project. It offers a unique and an interesting approach with potentially impactful results based on an energy-normalized cost of transmission.
- The project uses both survey data and internal analysis to develop cost models. Internal assumptions are checked and validated by the surveys, and the responses are validated by analysis. This dual validation system seems a positive way to "keep them honest" in both respects and therefore is good for building H2A schemes. Particularly interesting and important is the change in metrics for energy transport from cost per mile to cost per mile per energy unit.
- Much of the work performed brings a deep level of understanding of the costs associated with these technologies and uses. The work on energy transmission in particular is excellent, and both analyses have

the potential to provide insight into technological transformations needed to reduce the cost of hydrogen as an energy carrier and storage medium.

- Methods are sound and consistent with obtaining low-fidelity results, given limited budget resources. Investigators demonstrate good interactions with collaborators. Results of the energy transmission case study are intriguing and may warrant a much deeper dive using more data and more rigorous methods.
- The project demonstrates a very diverse effort with a deep technical dive. The derivations of project assumptions are well documented. The majority of the effort was directed toward the electrolysis work, but many assumptions were somewhat simplified with respect to scaling factors and cost savings between distributed and central scales. The project offers a good across-the-board comparison of energy transmission options.
- Investigators demonstrate strong methodology, knowledge of staff, and familiarity with DOE objectives and a breadth of technologies in the hydrogen space.
- The project is well organized and has a strong team. The questionnaire was a good start but needs to be simplified to improve responses.
- The analysis informs targets and explores new metrics for transmission.

Project weaknesses:

- Some assumptions appeared to be too high-level. The comparison of infrastructure pipelines may not have much use without context of the value of the final energy (e.g., comparison on a megawatt-hour basis without taking into account the efficiency losses of conversion). A simple introduction that explains why the comparison is being done and how the results will be used to steer project or Program end goals would be helpful.
- The weakness is the reliance on slow survey data from the industry. It is critical to have data, and it will be difficult to increase response rates, but more data would nonetheless help speed the project.
- The only weaknesses are the lack of quantity and reliability in the stack cost data on PEM/solid oxide and the subsequent lack of clarity on related uncertainties.
- More detail is needed on some of the assumptions used in the electrolysis analysis, particularly with regard to the lifetime of systems and the depreciation and durability limitations of the capital equipment used.
- The cost estimation methodology is so detailed that it is difficult to get a clear understanding of the critical performance metrics for a technology.
- Budgets seem high for this incremental and continued support to SA.
- The case is closed on PEM electrolysis. It seems that no matter how hard the commercial enterprise drives reductions in performance-enhancing hardware development costs, operating costs, or manufacturing costs, electricity costs nonetheless dominate. Unless and until this landscape changes, DOE should not be devoting resources to PEM electrolysis technology development, or the analysis thereof.

Recommendations for additions/deletions to project scope:

- The project team should consider ways in which the results from these studies could affect and drive further research and development in the science and engineering communities.
- Publication of the energy transmission results in a peer-reviewed journal is strongly recommended. The study team should subsequently carry out an expanded follow-up study to include both given energy production and transmission costs. The team should drop or defocus future PEC or STCH cost analysis efforts, since input data for meaningful study does not exist.
- More effort should be focused on analysis of biomass pathways. Regarding solar pathways, a definitive comparison of photovoltaics+PEM electrolysis and a comparison to PEC would be more impactful than updating STCH. The project team should consider how to put the results of each analysis into a learning rate model context, which is often the preferred context for discussing future costs of new technology.
- The project team should continue with future work to ensure as much industry input and review as reasonable within the scope of budget and resources available.
- Relative differences between PEM and alkaline in terms of capital, installation, and O&M should be shown.
- The project team should evaluate more scalable systems for water splitting, such as particle-based systems and possibly PEC. Furthermore, the team should work with laboratory experts to account for externalities and LCA and TCO.

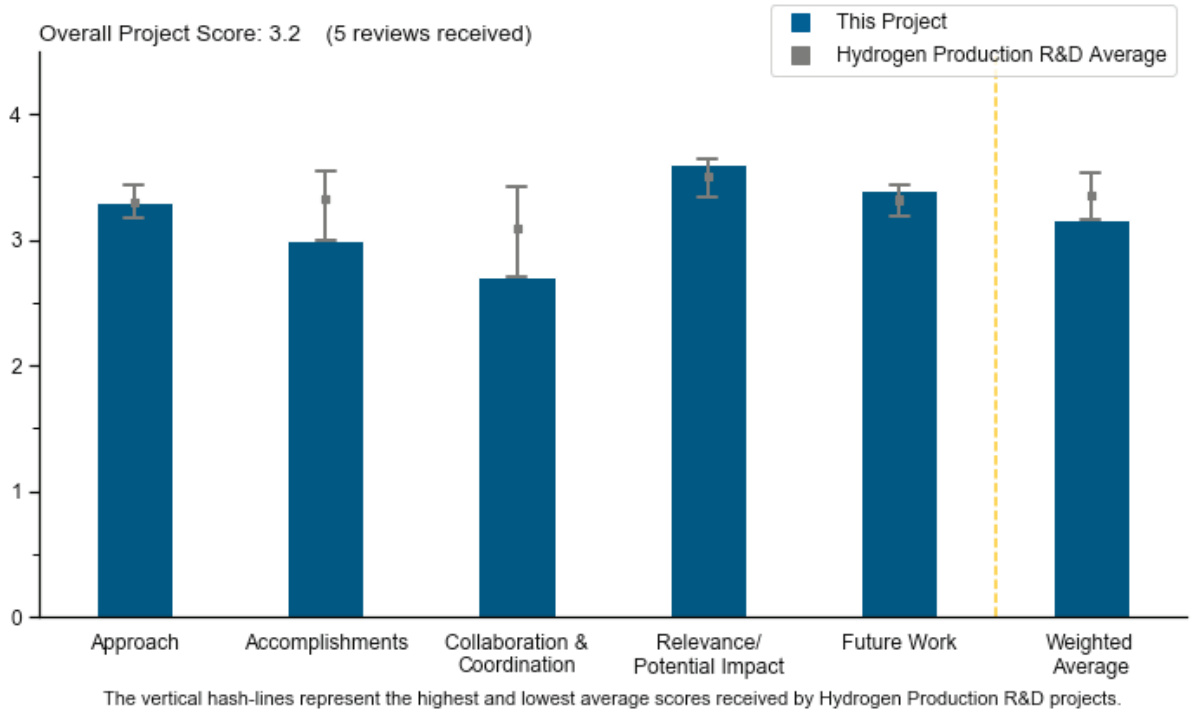
Project #P-143: High-Temperature Alkaline Water Electrolysis

Hui Xu, Giner, Inc.

Brief Summary of Project

This project aims to develop high-temperature molten alkaline electrolyzers with improved electrical efficiency and reduced cost. The electrolyzer will operate in the temperature range of 300°C–550°C. Specific project tasks include (1) development of porous ceramic oxide matrices, (2) incorporation of molten hydroxide electrolytes into the porous matrices, (3) selection of anode and cathode catalysts, (4) assembly and testing of single cells, (5) construction and testing of a 1.8 kW electrolyzer stack, and (6) system and economic analysis.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.3** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach to addressing the identified technical barriers is reasonable and logical.
- The project is well designed, feasible, and identifies and addresses critical barriers. The degree of integration with other relevant efforts is unclear. Short-stack efforts seem to be on the sideline. The reason for this is not apparent since single-cell progress is meeting targets.
- The approach of using molten salt electrolytes to increase electrolysis efficiency at elevated temperatures is good. This approach allows for obtainment of higher ionic conductivity and a potential for non-noble metal electrodes. Three major technical challenges to this approach are electrode materials, sealing materials, and corrosion. It is difficult to assess how effectively these challenges are being addressed. For example, the cell performance data used to meet the go/no-go milestone were obtained at 550°C; however, elsewhere in the presentation, it was stated that lower temperatures were needed to reduce corrosion issues. The lower-temperature data that were presented indicated substantially lower performance (confirming that electrodes were less active). Furthermore, button-cell testing (and presumably low steam utilization) was used to

collect performance data. Though button-cell testing is fine for assessing intrinsic performance, sealing issues are masked by using this method.

- Alkaline electrolysis promises lower cost due to lower cost of stack construction materials. However, there is usually a performance penalty compared to acid-based membrane systems. The higher temperature is expected to improve performance of the alkaline system. Matrix microstructure is correctly identified as a key parameter.
- The presentation suggests a good approach; however, the slides do not clearly lay out the approach. The milestones chart provides some information about the approach, but the previous slide is practically useless for understanding what the project team is doing to accomplish the targets.

Question 2: Accomplishments and progress

This project was rated **3.0** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Significant progress has been made toward the project objectives.
- Achieving good durability in this temperature range is quite challenging. Lowering temperature improves durability but also lowers performance to unacceptable levels. Performance improvements at lower temperatures appear to be going in the right direction. Resistance measurements should be reviewed and explained.
- Progress toward overall goals is sufficient. The team may need to increase spend rate and to return to short-stack efforts, as single-cell progress is meeting targets.
- Technical challenges have been identified, and progress has been made to address them. However, the investigators are already two years into a three-year project, and it seems that there is a long way to go to achieve the project's stated objectives. The original goal of demonstrating >90% lower heating value (LHV) efficiency in a stack appears to have been abandoned.
- Based on the milestone chart, the team has completed or is nearing completion of their goals. The slides do not do a good job of showing these accomplishments. Slide 20 suggests improvement at 450°C and suggests that the comparison to be made is on another slide. Given how much room is on the slide and the fact that this is a primary accomplishment, the comparison should be on one slide.

Question 3: Collaboration and coordination

This project was rated **2.7** for its engagement with and coordination of project partners and interaction with other entities.

- Interactions with the University of Connecticut have been very helpful. Their excellent images are very useful in understanding the materials.
- The collaboration with the University of Connecticut brings needed skills to the team. However, collaboration with a subsidiary company is not true collaboration. If Zircoa was simply providing off-the-shelf materials, then this does not seem like a collaboration either.
- Although the level of collaboration is sufficient, the investigators' communication of collaborative efforts requires expansion.
- Collaboration with an organization or company that may be interested in using the technology for hydrogen production is recommended.
- There is only one other collaborator outside of Giner, Inc., and its subsidiaries. Vendors are not collaborators. It would be helpful to provide details about the collaborators' data or information contributions in the Accomplishments slides.

Question 4: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- If both capital and operating costs can be lowered as predicted, it will lead to a significant reduction in production cost of hydrogen.
- The molten salt electrolyte concept is sound and has significant potential, if successfully developed.
- Impressive progress is made toward performance targets.
- The work is directly relevant to the goals of DOE regarding water splitting.
- This project aligns with the DOE Hydrogen and Fuel Cells Program.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The project offers a logical plan to further investigate lower operating temperatures and perform durability tests at 450°C. Transitioning the technology to a stack is important.
- The project's proposed future work is reasonable. More focus on corrosion issues and cell performance degradation is recommended.
- The future work seems appropriate.
- Based on the project's current stance, future work aimed at evaluating the newly discovered matrix material and optimizing performance at lower temperatures makes more sense than proceeding with stack development. Additional work performed to demonstrate sealing materials and approaches would be beneficial. A primary focus of additional testing work should be long-term durability of cell and seal materials (for durations much longer than 120 hours).
- Short-stack efforts require more comprehensive discussion and presentation.

Project strengths:

- The work up to this point shows substantial accomplishment. The project is fairly comprehensive, ranging from material stability to cost estimation.
- The project concept for increasing electrolysis efficiency is good. The electrochemical testing and discovery of new matrix materials are project strengths.
- Progress toward the performance target is excellent. Collaboration appears to be going well.
- The main project strength is its approach to addressing identified technical barriers.
- The team and the team's approach are good.

Project weaknesses:

- The presenter was very unclear about the results and when answering questions. Some slides displayed too many small, unreadable graphs, and other slides displayed incomplete datasets from which conclusions could not be drawn. This led to confusing statements and answers during the question-and-answer session. Specifically, it was unclear that the performance improvement at 450°C on slide 20 was being compared to data on another slide. The presenter was seemingly suggesting the performance was better at 450°C than 550°C.
- The project's main weakness is the investigators' choice to back away from the short-stack effort. Both processes should be approached in parallel (single-cell/short-stack development), particularly considering the remaining time and budget.
- The project requires an increased focus on technical "death threats." The project demonstrates limited technical progress toward achieving a viable materials set.
- The main project weakness is its lack of identification of or coordination with an organization or company that may be interested in developing the technology further after the project ends.
- The technique for resistance measurement needs improvement.

Recommendations for additions/deletions to project scope:

- Durability testing should be increased from a few hundred hours to 1000 hours.
- Focus on long-term durability and corrosion mitigation should be increased. Electrode performance should be assessed using impedance spectroscopy testing. Seal performance demonstration is necessary.

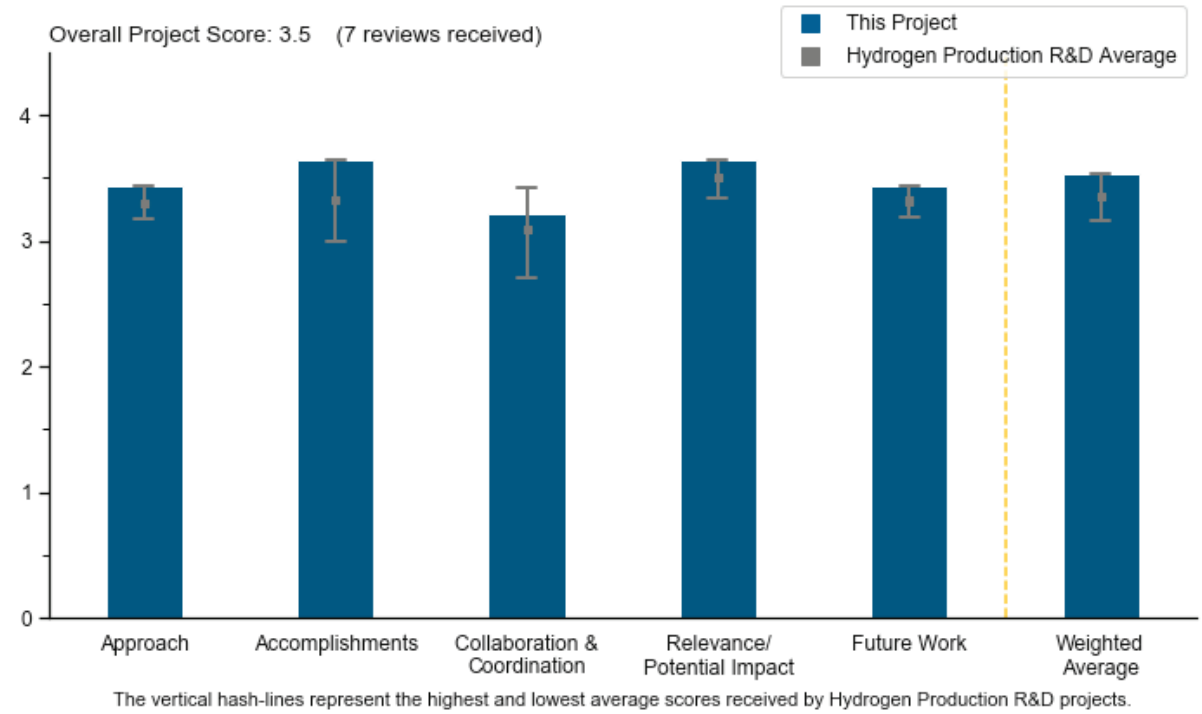
Project #P-177: Proton-Conducting Ceramic Electrolyzers for High-Temperature Water Splitting

Hossein Ghezel-Ayagh, Fuel Cell Energy

Brief Summary of Project

The project objective is to develop an advanced high-temperature water-splitting system for the production of hydrogen with a cost less than \$2/kg H_2 using a proton-conducting ceramic (P-SOEC) electrolyzer. The project targets improved cell and stack electrical efficiency (≥95% lower heating value [LHV] H_2) at current density >1 A/cm^2 at an operating temperature ≥500ºC. The project also seeks to reduce degradation to <1%/1,000 hours, showing a pathway to ultimately reach a stack lifetime of at least seven years. The cell area will be scaled up to 100 cm^2, and a stack with a capacity for producing more than 1 kg H_2/day will be demonstrated. A cell and stack manufacturing process will be developed that incorporates high-yield ceramic processing technologies.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- There are some compelling reasons to consider proton-conducting ceramic electrolytes for electrochemical water splitting to produce hydrogen. Temperatures are high enough that precious metal electrodes are not required in the electrodes, yet not so high that thermal integration is challenging. The ionic conductivity of proton-conducting ceramic electrolytes at 600°C can be similar to oxygen-ion-conducting ceramic electrolytes at 800°C. The electrode-supported electrolyte membrane architecture targeted in this project is a good way to minimize resistance (and power consumption) during electrolysis. A challenge is that the best proton-conducting ceramics (based on barium zirconate) require very high sintering temperatures for densification, which makes it difficult to achieve the targeted porous-electrode-supported, dense-thin-film electrolyte architectures. Another challenge is that the design of electrochemically active and stable electrode materials for operation at 600°C is not easy.

- The project demonstrates a comprehensive and balanced approach, and good progress has been made thus far.
- The approaches to addressing technical barriers and meeting milestones are reasonable and logical.
- The technical approach to achieving project objectives is well thought out and effective.
- The overall approach is very complete and promising.
- This work takes a logical developmental approach. Manufacturing medium to large proton-conducting membrane cells is difficult. Converting the cells to a stack is even harder. It is unclear where the innovation is or if the approach will be successful. The investigators' proposal is similar to other unsuccessful projects done in the literature.
- The area for the tall stack with a capacity of 1 kg H_2 per day should be roughly estimated based on the targeted current density and stack efficiency. A stack lifetime longer than seven years is one of the project objectives; therefore, an appropriated estimation approach is needed.

Question 2: Accomplishments and progress

This project was rated **3.6** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The researchers achieved outstanding achievements within the short term of this project thanks to their strong research background in this field. The achievement so far guarantees the success of the overall project objective and DOE goal.
- Excellent progress has been achieved, and several milestones have been completed ahead of schedule.
- Significant progress has been made toward project objectives.
- The project is off to an excellent start.
- Excellent progress has been made toward fabrication of the co-sintered membrane architectures. It will be interesting to observe whether similar microstructures can be obtained on larger area and stack intent cells. The degradation of the steam electrode may be problematic. This degradation will need to be addressed for the project to survive its first go/no-go milestone.
- The project goals are on track. The project should evaluate the degradation during thermal cycling.
- This project is just starting; therefore, investigators reported mostly plans and data from previous work. The initial data looks interesting.

Question 3: Collaboration and coordination

This project was rated **3.2** for its engagement with and coordination of project partners and interaction with other entities.

- Close collaboration with other institutions and partners is demonstrated. This collaboration has produced results that are important to achieving the objectives of the project.
- The project demonstrates reasonable and balanced contributions from collaborators.
- This project is a good example of collaboration between university and industry. The inclusion of national laboratories would improve this collaboration even further.
- Interactions between collaborators are reasonable.
- This project has three team members, although it could be argued that a wholly owned subsidiary of Fuel Cell Energy (FCE) should be considered as a separate team member. There does not appear to be interaction with other organizations, although at this stage such interactions may not be necessary.
- Investigators are collaborating with Colorado School of Mines (CSM). CSM provides some good materials but has been unable to scale up. FCE is skilled at scaling up, so this collaboration makes sense. It is not clear why investigators list Versa Power Systems (VPS) as a collaborator since VPS is owned by FCE.
- The way in which the fabrication effort is coordinated with VPS is unclear.

Question 4: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- Solid oxide electrolysis is a key component of DOE's emerging portfolio of hydrogen production technologies. FCE has demonstrated solid oxide fuel cell (SOFC) stacks and systems at very large scales, and if this project is successful, FCE will be positioned to complete system development and ultimately produce large-scale solid oxide electrolyzer systems. Thus, this project has high relevance and a significant potential impact.
- High-temperature electrolysis is very important to H2@Scale. It does not require the expensive materials (Pt and Nafion) used by low-temperature electrolysis, and it requires less electricity. If the investigators can get the proton-conducting membranes into reasonable (>100 cm^2) cells and stacks, the achievement may have a large impact. The lower operating temperature of proton-conducting membranes enables the use of lower-cost metals for the interconnects and should have lower degradation.
- The proposed current density, operating temperature, long-term durability, hydrogen production scale, and efficiency can potentially help to move toward DOE's target of $2/kg.
- This is a very important, very high-impact project.
- The project is relevant to high-temperature water electrolysis.
- The project aligns well with the Hydrogen and Fuel Cells Program (the Program) and DOE research, development, and demonstration objectives.
- The project aligns well with the Program.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- Much remains to be done, but progress thus far is impressive. The future work outlined is possible, given time and budget.
- Plans clearly build on past progress and are sharply focused on critical barriers to project goals.
- The proposed future work is excellent. It would be helpful for the team to include the methodology they used to predict a stack lifetime longer than seven years.
- The proposed future work is a logical continuation of the presented effort. Thermal cycling should be included in future testing.
- The three focus areas of future work are acceptable. Stabilization of the steam electrode is critical. It appears to be a fundamental materials problem, and new materials sets may need to be explored.
- The investigators must demonstrate that they can build cells and stacks with good performance.
- The approaches to be used to improve cell Faradaic efficiency and reduce cell performance degradation are unclear.

Project strengths:

- This project demonstrates a balanced and systematic approach to each facet of the protonic ceramic fuel cell/electrolytic cell and stack manufacture. The project draws on vast experience and institutional knowledge from collaborators. The team appears very solid. Manufacturing defects are low, and cell strength is high.
- The main strength of the project is the complementary expertise of the team members: FCE, CSM, and VPS.
- The team has experts in proton-conducting membranes. If the team is able to manufacture the cells and stacks, it will be very impactful.
- The project has been effectively planned and well executed, with good progress achieved.
- In general, the project achieved excellent progress in the short term, which is very promising.
- The project benefits from its use of FCE's proven and scaled-up SOFC stack platform.
- The project is well structured and holistic.

Project weaknesses:

- There are no obvious weaknesses.
- A more explicit discussion and characterization of cell and stack leak rates is needed and would offer a substantial addition to the project. Since performance and progress are impressive and cell strength is high, sealing should not be an issue.
- Cell degradation in the fuel cell mode seems to be a challenge. Some effective approach may be needed to achieve the project milestones set for degradation rate.
- The degradation of the steam electrode must be addressed.
- Investigators' anticipated future testing lacks thermal cycling.
- It is hard to see what the innovation is in cell and stack manufacturing that will allow larger cells and the assembly of the cells into a stack.

Recommendations for additions/deletions to project scope:

- A greater focus on cell leaks, stack leaks, and source tracking is recommended.
- The steam electrode degradation needs to be addressed. Project focus on this issue should be increased before expending resources on other project activities.
- The investigators should distinguish between current progress and literature data.
- Greater effort should be directed toward materials stability and durability under operating conditions.
- There are no recommendations for additions/deletions to project scope.
- No additions or deletions are recommended.

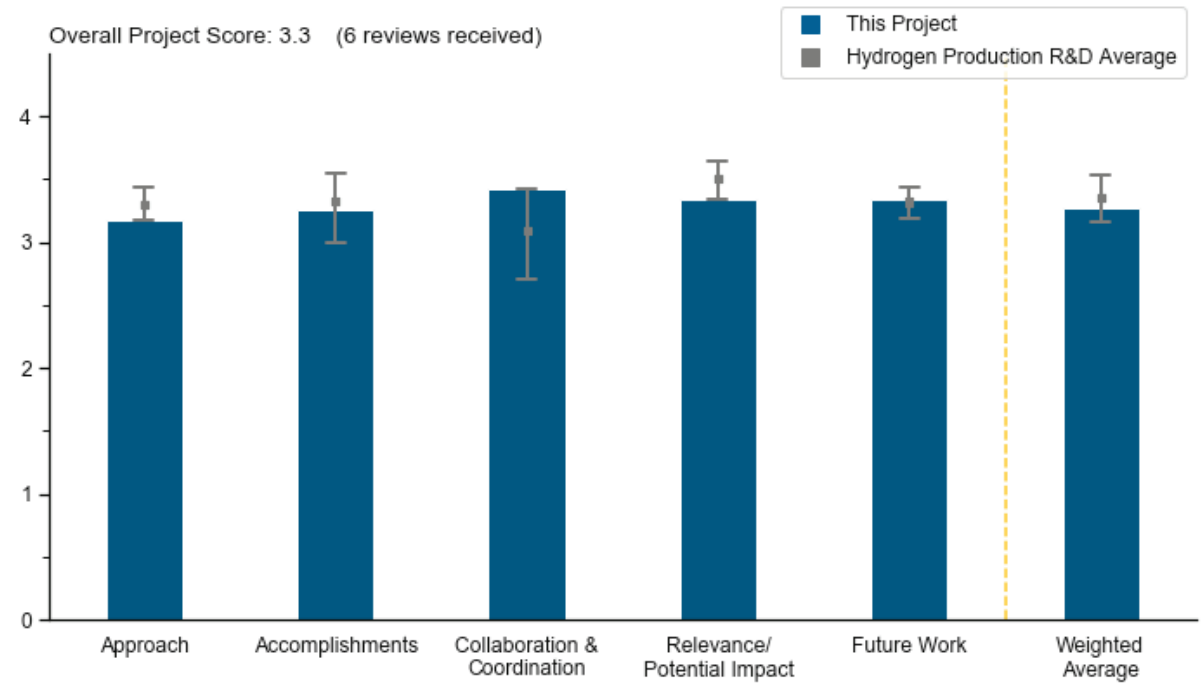
Project #P-178: Industrially Scalable Waste Carbon Dioxide Reduction to Useful Chemicals and Fuels

Todd Deutsch, National Renewable Energy Laboratory

Brief Summary of Project

The goal for this project is to develop an electrochemical reactor that accelerates the rate of the limiting reaction steps for converting CO_2 into liquid fuels and valuable chemicals so that the device operates at power densities commensurate with the rate of point-source CO_2 emissions. This new reactor utilizes a CO_2–water electrolyzer that stores inexpensive renewable electricity as hydrogen and carbon bonds in these products. This device has the potential for improved energy efficiency, chemical selectivity, and throughput compared to conventional thermochemical processes. The project addresses technical barriers through (1) CO_2 mass transport limitations for reduction current density; (2) advanced membranes and membrane architectures (e.g., bipolar membranes); (3) Ni-P catalyst development; and (4) in situ electrochemical component integration.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Production R&D projects.

Question 1: Approach to performing the work

This project was rated **3.2** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The project and its approach are ambitious in simultaneously tackling four significant problems. The approach is described succinctly and logically. Coupling experimentation with modeling is a good practice, and the use of modeling from the very beginning is wise. The approach does not rely on material breakthrough but rather on rational combination of materials, structures, and logical approaches.
- This project focuses on electrolyzer design, a critical component for realizing large-scale CO_2 conversion technologies. Components such as membrane, flow field configuration, and catalyst loading all impact the overall cell performance and Faradaic efficiency. A thorough effort is needed to understand how all these parameters work together. Furthermore, optimization is needed. The National Renewable Energy Laboratory (NREL) is leveraging its extensive expertise and capability in water electrolyzer design to

create a benchmark technology for CO_2 electrolysis. NREL is also pursuing 2D modeling (e.g., COMSOL and Fluent) to clarify the roles of mass transport of products and reactants, liquid water flow, electrochemical reaction kinetics, and charge and heat transfer on device performance. NREL is also leveraging other X-ray characterization capabilities at Argonne National Laboratory (ANL) for nanoscale synchrotron X-ray computed tomography (nano-CT) to analyze catalyst and electrode structure. Finally, Rutgers University will develop nickel phosphide (NiP) catalysts for the cathodic CO_2 reduction reaction. Rutgers University has reported that this NiP catalyst can produce C1–C4 liquid products at very low over-potentials, but it appears to produce significant H_2 at larger applied potentials. This could be problematic to achieving high current density and desirable product selection. The initial six months show good progress with the construction of a contained CO_2 electrolysis test station. Further work will incorporate product detection using mass spectrometry. However, quantification of gaseous products is typically done with gas chromatography (GC), so future efforts will require incorporating in-line GC for real-time analysis and quantification of product formation rates, selectivity, and Faradaic efficiency.

- The project approach is good. Most important barriers are identified (slide 4) and addressed by some effort. The approach can be strengthened by performing a rough assessment of the largest rate-limiting steps such that efforts may be directed in proportion to relative size of limitation. The assessment would also be useful to inform systematic study. As an example, it is difficult for the reviewer to determine the relative magnitude of CO_2 solubility limitation as compared to the impact of water management. It is likely that the range of possible current densities is small enough to render a passive water management scheme sufficient under most or all applications. The team reports that a model has been developed and is to be published (slide 8), but it would be reasonable to report some preliminary results to reviewers to allow for recommendations regarding the overall approach going forward.
- The conversion of waste CO_2 to useful products is a clearly identified objective. The barriers related to mass transport, membrane, catalysts, and component integration are well identified.
- The stated research and development (R&D) approach, especially regarding the improvement of mass transport via the use of gaseous diffusion electrodes and membrane electrode assembly (MEA), sounds reasonable. Also, starting with known CO_2 reduction catalysts makes sense. It appears that the team's approach is to carry out two distinct electrochemical processes, CO_2 reduction and H_2O oxidation, in a single cell. This approach may not be the most effective approach, given the early stage of knowledge of these systems. Instead, the team might initially consider a two-step approach in which hydrogen (from the well-understood water electrolysis system) is fed to a separate CO_2 electrolyzer to systematically isolate parameters and gain mechanistic understanding of the various steps.
- The approach is not defined. It seems that investigators will build a test stand, but investigators did not specify what products they will be making. The catalysts were not identified. Furthermore, there was no experimental plan. It is good that the investigators plan on modeling, but without specific products and conditions, it is unclear what they will be modeling. The innovations described relate to improving the CO_2 transport and using a non-platinum-group-metal catalyst. However, it was anticipated that the CO_2 transport would use hydrophilic and hydrophobic channels, which is a variation of what is already being done in polymer electrolyte membrane fuel cells. It is not evident that investigators can achieve significant advancement in the state of the art with their approach. The approach incorporated no technoeconomic analysis. Investigators failed to identify and address the key challenge to CO_2 reduction. In their model on slide 8, they identify synthesis gas and methane as products. However, thermochemical conversion of CO_2 to synthesis gas and methane is already well established in the literature. It is very unlikely that a low-temperature electrochemical approach will be more efficient and less expensive than current state-of-the-art thermochemical production. When asked about their choice to produce synthesis gas and methane, investigators stated that they did not plan to produce synthesis gas and methane but, in fact, plan to produce other products. If this is the case, it would be beneficial for the investigators to list the products they actually plan to produce and eliminate time spent developing models that make products the investigators do not intend to make experimentally.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team's achievements are substantial, given that the project is still in its early stages. The project has already demonstrated improved polarization from catalyzed electrospun electrodes. The multiphysics model is useful for conceptualization and prediction of operational metrics. The development of a custom electrolysis test stand shows ingenuity and creativity.
- The team has made good progress in the first six months of the project timeline. The project has constructed an electrolyzer test station with controlled humidity and fluid and gas delivery systems. The test station will harness the capability of an in-line mass spectrometer to detect products formed at the cathode. Team members have met the Quarter 1 (Q1) and Q2 milestones. The Q3 milestone is on track, and the go/no-go decision points in Q4 seem reasonable.
- The team has made good progress in dealing with materials that are difficult to electrospin. Substantial effort was required to achieve MEA production using the low-throughput electrospinning approach.
- The team's progress toward the milestones appears satisfactory. The system is operational, with needed safety and automation.
- The project is too new to produce meaningful accomplishments, but it is off to a good start. It will be interesting to see how the project develops between this year and the next.
- It took the team five months to build the test stand, begin developing models, and produce samples. Given the time and budget, this is a reasonable amount of progress. The team should have identified the first products and reaction conditions to be evaluated and modeled.

Question 3: Collaboration and coordination

This project was rated **3.4** for its engagement with and coordination of project partners and interaction with other entities.

- This project demonstrates good collaboration with other national laboratories and with Rutgers University. NREL has taken the lead with its development of the electrolyzer hardware and test station. This development includes building the CO_2 electrolyzer and verifying its performance, an endeavor that suits the laboratory's expertise in water electrolysis device construction and operation. NREL is constructing the ionomer and bipolar membrane, as well as fabricating the gas diffusion electrode (GDE) and MEA. NREL will conduct modeling to determine how each component of the electrode affects system performance. Los Alamos National Laboratory (LANL) will contribute to the project by developing advanced cathode structures. LANL will also conduct nano-CT characterization of the electrode–catalyst structure. Rutgers University is responsible for developing the NiP catalyst to incorporate into cathodes.
- The project has a very strong team of collaborators that include experienced individuals and organizations. Team members are funded at substantial levels commensurate with their contributions.
- The team appears motivated and collaborates well.
- LANL, ANL and Rutgers University are strong partners that bring much value to the team. Based on the presentation, it appears the project innovation is coming from the team members. The poster should distinguish between NREL's partners and the groups with which NREL is coordinating. For example, the poster lists LANL as a partner but also lists other parts of NREL as partners; however, it is assumed that these other parts of NREL are merely groups with which NREL is coordinating.
- Collaboration among the national laboratories and Rutgers University looks good. That said, the team should also seek industry input to strengthen the project.
- Investigators demonstrate adequate collaboration and coordination. However, since there is no collaboration with industrial partners, the team may be missing out on the industrial perspective.

Question 4: Relevance/potential impact

This project was rated **3.3** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- The field needs a standardized testing station technology for catalyst benchmarking and confirmation of performance. Currently, most laboratories have their own electrolyzer devices that may or may not use standardized components. This makes comparison between different groups and reports extremely difficult. This project will address this challenge by developing a standardized testing architecture for evaluating catalysts and verifying system performance.
- The project has the potential to enable an entire class of reactors applicable to many synthesis pathways. The project is directly aligned with DOE goals to reuse waste CO_2 as a pathway to lowering overall CO_2 release into the atmosphere.
- The project demonstrates a high-impact, reasonable approach.
- The project is relevant to CO_2 utilization efforts. The principal investigator should ensure that results can be translated into industrial processes by including fundamental scientific details.
- The project is aiming to develop an electrochemical process that "…could greatly improve the energy efficiency and selectivity compared to thermochemical processes starting from water and CO_2." However, this benchmark may not be very meaningful since there are no such commercial thermochemical processes for comparison. Instead, benchmarks should include known processes with renewable energy input, either as direct electricity use or hydrogen via electrolysis. In other words, this project (and other upcoming e-fuel concepts) need to demonstrate the most efficient and sensible use of renewable energy, i.e., an existing process such as direct use, battery storage, or hydrogen or new processes such as converting $CO_2 + H_2O$ back to hydrocarbon fuels or chemicals.
- CO_2 reduction has historically been achieved by DOE Basic Energy Sciences and Fossil Energy programs. It is unclear how this project distinguishes itself from those other programs. Since investigators did not identify what products they will make or what catalysts they plan to develop, it is difficult to provide feedback on the potential impact. While the reuse of CO_2 may be impactful, it is difficult to determine the extent of the impact without a technoeconomic analysis. The analysis should compare the cost of producing the target products electrochemically versus thermochemically. Investigators should include the market size along with other relevant factors in their consideration.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The project demonstrates a thorough assessment of future work. It may be useful to determine the impact or cost of separation of the large product distribution on the overall process. That is, operation at low current density with a very narrow product distribution may offer substantial advantages over higher current densities and broader product distribution. Impact could initially be determined using a separate model. It is recommended that investigators attempt to increase overall pressure of operation to allow for CO_2 concentration control while maintaining pressure balance across membranes.
- The team plans to complete an electrolyzer testing station with incorporation of mass spectrometry. The team also plans to demonstrate technology with NiP electrocatalysts on a GDE cathode. The progress on milestones and go/no-go decision points in Q4 will determine whether the project continues. From there, the team will be able to begin benchmarking catalysts and confirming the performance of novel catalyst materials. Challenges will likely occur when translating the performance of aqueous cell catalysts into an operating electrolyzer MEA architecture. These challenges will become apparent only once full testing has begun, and electrode/catalyst characterization will likely identify mitigation strategies to overcome these challenges and improve system performance.
- The proposed future work sounds reasonable based on the limited data so far. Understandably, at this point, the project is too new to propose data-driven actions.
- The proposed future work is satisfactory.
- Considering that most of the project lies ahead, the team's proposed future work is quite broad.

- The proposed future work is vague; more specificity is required. Though the investigators propose to "build more CO_2 test stations" and "test catalysts in MEAs," it is unclear which catalysts and membranes they intend to use and what the innovation will be. Investigators should identify the number one challenge limiting electrochemical CO_2 reduction and determine how to meet this challenge. Their current plan does not do so. Investigators need to identify what their target molecules are and why. They should also include a technoeconomic analysis to justify their work.

Project strengths:

- The project demonstrates impressive achievement, considering that the team has been under contract for less than six months. The project plan is well constructed and ambitious. The team is very strong in the relevant technical areas.
- This project will establish a standardized testing platform to benchmark and evaluate catalyst performance. This is certainly needed in the field. The project leverages the excellent capabilities of NREL, ANL, LANL, and Rutgers University.
- The project appears to be well positioned and focused to tackle the key technical aspects of improved catalyst and membrane developments.
- The project offers a multidimensional approach.
- The project is supported by a large budget and good partners.
- The project is high-impact.

Project weaknesses:

- The project's only real weakness may be the choice of catalyst. For example, the chosen catalyst has been demonstrated to produce a variety of liquid products at very low over-potentials, but H_2 evolution will become an issue at larger applied potentials. The team may need to consider a catalyst with a less complex product distribution for initial electrolyzer testing, evaluation, and electrode optimization.
- The list of factors that affect operation must be refined. The experimental space is vast, so it is necessary to pare down the variables to be studied. Several of the R&D challenges listed on slide 4 may be eliminated without affecting the outcome of the project. These may be revisited after the technology develops further.
- The project lacks industrial collaboration. In the absence of an industrial viewpoint, the team may develop technology that may not translate into industrial practice.
- The project's weaknesses are related to lack of system-level considerations, such as the lack of an appropriate reference system for benchmarking, insufficient overall cell or system mass and energy balance discussions, and gas separation or recycling challenges due to likely non-ideal CO_2 conversion efficiency.
- Investigators do not address the key limitation to room-temperature CO_2 reduction. Their experimental plan is extremely vague. Investigators do not justify the work they are doing with technoeconomic analysis. They do not identify materials, catalysts, or products to be made. However, the characterization the team plans to do looks to be very good.
- There is insufficient discussion of performance projections and metrics for success. A target or expected product compound is not clearly stated.

Recommendations for additions/deletions to project scope:

- The project forms an excellent basis to assess the performance and functionality of the basic concept. If positive results are shown, the scope of the project should be expanded to other catalysts.
- The team should use the model and verify its results experimentally to remove factors that make little impact. The team should also consider scaling up the electrospinning setup.
- The term "waste CO_2" should not be used, as it can be misleading. The term gives the impression that CO_2 is free, or even available at negative prices. The clear majority of CO_2 byproduct that enters the atmosphere comes in the form of very dilute concentrations that require additional processing and significant capital investment to achieve the pure form used as feedstock in such electrochemical systems. In fact, the high cost of concentrating and capturing CO2 can potentially be a showstopper in the economics of most commodity-type utilization and conversion processes. CO2 may be undesirable, but it is almost certainly not cheap.

- Investigators need to identify what products they are targeting and provide a technoeconomic analysis showing that those products can be reasonably synthesized. NREL has excellent technoeconomic analysis capabilities, so it was surprising that they were not included in the project. The project needs to develop an experimental plan in addition to the test station construction plan. Additionally, the team needs to improve the model approach. There has been extensive reaction and reactor modeling of CO_2 reduction, and it is not clear that this literature is being used.

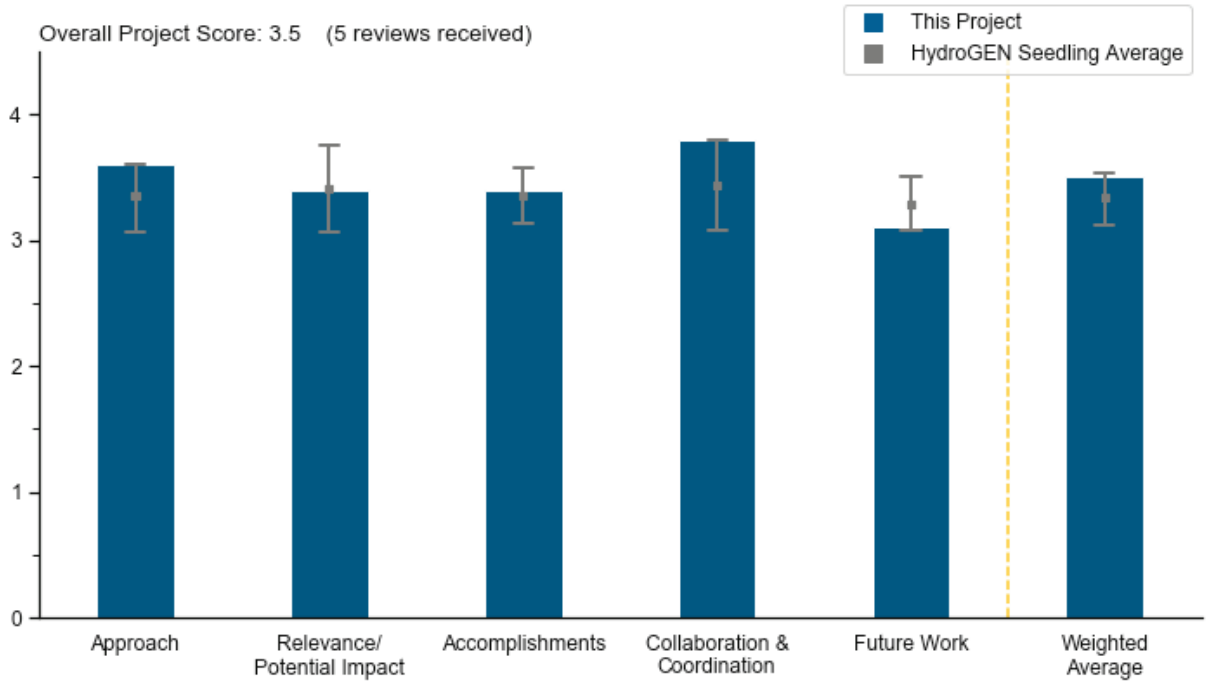
Project #P-148: HydroGEN Overview: A Consortium on Advanced Water-Splitting Materials

Huyen Dinh, National Renewable Energy Laboratory

Brief Summary of Project

The HydroGEN Consortium's objective is to facilitate collaborations between federal laboratories, academia, and industry to evaluate and accelerate the research and development (R&D) of innovative, advanced materials that are critical and necessary to advanced water-splitting technologies for clean, sustainable, and low-cost hydrogen production. Water-splitting technology pathways supported by HydroGEN include (1) photoelectrochemical (PEC), (2) solar thermochemical (STCH), (3) low-temperature electrolysis (LTE), and (4) high-temperature electrolysis (HTE).

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.6** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The approach is strong and targets key areas in PEC, STCH, and LTE and HTE to achieve the U.S. Department of Energy (DOE) target of $2/kg. The consortium's offered capabilities in synthesis, characterization, and theory and computation are clearly an invaluable asset to consortium participants. There are multiple layers of engagement with participants and collaborators across capability nodes, the Energy Materials Network, and the Data Hub and ample opportunities for collaboration, with many accomplishments already. As the consortium matures, it may be helpful to establish formal internal mechanisms for self-assessment, deciding future directions, identifying existing barriers, and selecting concrete steps to take to overcome these to maximize the impact of the nodes and ensure adaptability. It was unclear whether such mechanisms exist (perhaps through the steering committee) to set strategy to ensure a continued effective approach.

- The consortium is aiming to reach $2/kg of hydrogen, and various technologies are going to be used to reach this target: from PEC to STCH and LTE and HTE. This project's approach is surely going to open a wide range of possibilities to reach that goal. This shall also be facilitated by using cross-cutting innovation and theunique capabilities found in the 80 nodes within HydroGEN. The task to coordinate and organize information in a multinode platform shall guide the scientists to reach their specific targets and to properly compare the achievements.
- The project appears to be well managed, with excellent collaboration among the six national laboratory partners. Through its nodes and the Data Hub, HydroGEN makes available a wide range of unique national laboratory capabilities, expertise, and data that support the development of the four advanced water-splitting technologies being pursued. The initiation of the supernodes, which help to support R&D efforts within the partner laboratories in their areas of technical expertise, should provide significant additional "value" to HydroGEN toward meeting the DOE hydrogen production goal of $2/kg.
- This effort appears well structured to leverage DOE dollars by combining expertise residing in different national laboratories and aggregating the knowledge from different groups to solve materials challenges.
- HydroGEN is more of a program than a project. The structure is very well defined, and the partners are very well connected. It is of very high value that a wide range of different technologies are combined, which helps with understanding other technologies and identifying synergies between them. The project management seems to be very efficient. The communication structure is close and seems to work very well. However, the size of HydroGEN makes it difficult for all partners to be aware of all developments.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- To meet the DOE hydrogen production price goal of $2/kg, HydroGEN and its focus on developing advanced water-splitting technologies for producing cost-competitive hydrogen are critical to DOE and the Fuel Cell Technologies Office (FCTO), given that many of the companies involved in some aspect of these nascent technologies do not have the resources available to pursue the level of fundamental R&D necessary to make these technologies commercially viable. Through its "node" approach, HydroGEN leverages and makes available the collective unique capabilities and expertise of its partner national laboratories to the broader scientific community, which should help accelerate the development of these technologies.
- Advancing electrolysis systems for energy conversion and storage can be achieved only by substantial innovation in materials synthesis. Only by demonstrating novel materials will the goal of $2/kg be achieved. Therefore, with select expertise and unique capability aligned with strong collaborative work, a substantial impact and relevance in the field of hydrogen production is expected.
- According to the website, a majority of the nodes are being used, which shows engagement with the community toward helping DOE reach its targets. The consortium can point to several technical accomplishments, as well as a dedicated effort toward benchmarking, all of which are very valuable. Activities are distributed broadly across a variety of R&D areas, and many of the individual projects already cite several notable technical achievements toward the hydrogen targets. One challenge in assessing impact is that it is a little difficult to assess the specific, concrete contributions of the nodes toward helping the projects meet these targets (that is, whether node involvement is generally critical, important, or tangential to project success). While making this assessment is rather challenging, it may be useful to identify clear examples or evidences of how the nodes have affected the progress of the individual R&D efforts.
- By managing the materials characterization within the national laboratory complex, HydroGEN helps industrial–academic teams focus on making progress toward their performance and durability targets.
- HydroGEN is strategically focused on materials development to achieve faster breakthroughs in this key area. The project is very strong in this respect. However, cost reductions will not be determined by reactive materials, in the end, but by land use, receiver and reactor efficiencies, and the market. These parts are nearly not covered in HydroGEN. Taken the timeline for implementing renewable hydrogen production, it seems to be difficult for HydroGEN to provide the necessary fast input for the already growing market. If there are no machines that produce hydrogen, even with less efficient materials, better materials will never make it into application.

Question 3: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The consortium's suite of accomplishments is quite impressive, and the members are clearly enabling a diverse set of activities around advanced water-splitting technologies. Specifically, the consortium is to be commended for the level of involvement of the core laboratories in HydroGEN activities via the nodes and now the supernodes, which was evident throughout the presentations. The visibility and accessibility via the website are high. The establishment of the standard technology transfer agreements between consortium partners will be a very useful approach to streamline access and overcome a common barrier. The establishment of the supernodes to merge capabilities is also a valuable asset. Finally, the benchmarking effort for materials characterization supported by the consortium will be very useful moving forward, especially for assessing progress toward targets. The establishment of the HydroGEN Data Hub and its degree of utilization within the consortium are solid, and clearly a good deal of effort has gone into making the Data Hub accessible and user-friendly through the development of interfaces, visualization tools, etc. As the Data Hub grows further, additional metrics beyond the number of files uploaded may be useful in assessing the impact and value added of the Data Hub itself. These could be, for example, the extent to which data are being shared among different consortium members or cited in forthcoming publications.
- The project is still in its initial phase. However, substantial progress can be observed by the number of contributions to the Data Hub and the volume of data already available. It is also very interesting to see the number of high-quality seedling projects applied for and approved within the consortium. Progress over the initial phase is also showing. Within a few seedling projects, a few milestones have been already achieved, showing that the consortium is on excellent track toward achieving and reaching the proposed goals.
- HydroGEN's overarching mission aligns well with FCTO's mission to develop renewable hydrogen production technologies capable of producing hydrogen at $2/kg. The accomplishments presented for each of the four water-splitting technologies appear to demonstrate good to excellent progress, although it is very difficult to put into perspective how much these accomplishments are moving the needle toward meeting the DOE production goal of $2/kg of hydrogen for the individual technologies. One of the major challenges for HydroGEN is that while its $22 million in funding is substantial, it is a challenge to determine how to best allocate its funding across four distinctly different water-splitting technologies. Based on five funding opportunity announcement awards for each of the four technology areas, it appears that FCTO is showing no "favoritism" toward one technology or another, which is understandable at this early stage. However, as HydroGEN moves toward its renewal, FCTO, along with HydroGEN, should do a "deep dive" to evaluate the state of each technology toward meeting the DOE target, as well as the technology's market readiness, to decide how to best allocate its limited funding.
- As the project is so big, there must be differences between the seedling projects. Not everything can be outstanding. However, the progress reported is excellent. None of the technologies seems to be on a dead-end road, and all showed how their developments can potentially contribute to the goal of $2/kg hydrogen very well.
- From this presentation, it is challenging to assess progress measured against performance indicators. The go/no-go decision points and criteria are not mentioned in the slides.

Question 4: Collaboration effectiveness

This project was rated **3.8** for its collaboration and coordination with HydroGEN and other research entities.

- The structure of HydroGEN is really impressive. The projects are very well connected. A benchmarking process is established. The Data Hub is the perfect vehicle to allow the whole consortium to interact with each other and get value from the achieved results. The reported communication between the partners in the projects, and also between the projects, is outstanding. It is fantastic to observe how HydroGEN supports the different communities growing together.
- The HydroGEN Consortium is clearly valuable to the research community, particularly to academic partners who are obviously benefiting from the capabilities of the core laboratories in synthesis, characterization, and theory and computation. There is substantial visibility through the website, which

makes capabilities clear and has clearly resulted in good utilization of laboratory capabilities among HydroGEN participants. Efforts at facilitating collaboration via the Data Hub, the benchmarking efforts, and the streamlined technology transfer agreements show targeted efforts to engage the community.

- Based on the testimonials, there appears to be significant benefit to the broader scientific community's ability to access the expertise and capabilities of HydroGEN's partner laboratories through the nodes. One of the project's key activities is the development of benchmarking protocols that will provide the basis for evaluating and comparing the performance of the new materials toward meeting the FCTO technical targets, using well-defined experimental approaches and metrics that allow for a fair and unequivocal comparison. There has been a significant increase in the cumulative data added to the Data Hub, as well as in the number of HydroGEN members participating over the past year, although it does appear that the vast majority of data added was around the time leading up to and including last year's Annual Merit Review. While the type of experimental data added was presented, it would be interesting to know to which technology the data added aligns. It would also be interesting to know if members of the broader scientific community who are not members of HydroGEN find the data, as presented and available in the Data Hub, useful and of value. Given that platinum-group-metal (PGM)-free oxygen evolution reaction and hydrogen evolution reaction catalysts for LTE is one of HydroGEN's major focus areas, it would be interesting to know the extent to which HydroGEN is collaborating with and able to leverage the R&D being conducted in ElectroCat, whose mission is to develop PGM-free catalysts for polymer electrolyte membrane systems.
- Within the results presented, the strong collaboration between the project partners and other R&D peers across the community is clear to see. However, it is recommended that a list of achieved publications be presented, so that the multi-laboratory collaboration within HydroGEN and with other institutions can be easily identified.
- The National Renewable Energy Laboratory appears to effectively facilitate interaction between teams and HydroGEN nodes. Working groups help to foster exchange among similar projects.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The project's proposed future effort continues to coordinate the many parallel efforts and integrate the research. Benchmarking to quantify the progress of each competing technology will be very important.
- The proposed future work is logical and will be the right way to efficiently achieve the goals. However, as HydroGEN is so big, it is difficult to follow everything in every project.
- On the whole, the proposed future activities are a logical and reasonable continuation of ongoing efforts. HydroGEN shows solid efforts to continue and expand their ongoing activities. Some proposed activities shown, such as "integrate the whole system," are a little vague, and it is not clear what concrete steps are to be taken for this integration or how they have been determined. Similarly, for the proposed activity "Continue to develop a user-friendly, secure, and dynamic HydroGEN Data Hub," it is not clear what aspects of the Data Hub will be targeted in the short, middle, and long terms.
- Much of the proposed future work lacks focus and distinct metrics or goals. It is not clear what "integrate the whole system" means toward accelerating the R&D of HydroGEN. Likewise, the "collaborate and perform integrated research in the five supernodes" lacks focus and goals or objectives. The establishment of benchmarking standard protocols is a critical aspect of this project. Given that HydroGEN is nearing the end of its initial funding period and is probably up for renewal within the next year or so, it was expected that one future work action would have been to begin to develop the framework for the next phase of HydroGEN.
- The project's proposed future work is excellent, but it is not clear how the proposed tasks are going to be implemented.

Project strengths:

- HydroGEN has a logical and very well-established structure. It clearly helps strengthen communication between different scientific communities. Therefore, it is the perfect tool to bring together researchers with different backgrounds and create synergies. This will help overcome problems faster. The exchange of data

is outstanding. It gives all participants the possibility to act faster and to put results in this large framework. The benchmarking is very important and will help with following the actions and results efficiently.

- The project appears to be well managed, with excellent collaboration among the six national laboratory partners. Through its nodes and the Data Hub, HydroGEN makes available a wide range of unique national laboratory capabilities and expertise, as well as data that supports the development of the four advanced water-splitting technologies being pursued. To date, there appears to be good utilization of the nodes. The initiation of the supernodes, which help to support R&D efforts within the partner laboratories in their areas of technical expertise, should add significant additional value to HydroGEN in meeting the DOE hydrogen production goal of $2/kg.
- The project's strengths include its ambitious target, the expertise among the different players within the consortium, the team's unique capability to perform the proposed tasks, the awareness to create a user-friendly and super-necessary R&D information platform (Data Hub), the ability to perform cross-cutting R&D among laboratories, the awareness of the necessity of a solid benchmark, and the ability to achieve fast results.
- The project's strengths include its effective and dynamic collaborations that engage laboratories in R&D activities toward DOE hydrogen targets. The project's further strengths include the community-building efforts through the Data Hub, the benchmarking efforts, and the expertise and capabilities of the laboratories.
- The project manages a complex effort of coordinating many researchers and different technologies for hydrogen production at varying technology readiness levels (TRLs).

Project weaknesses:

- It is difficult to put in perspective to what extent the accomplishments presented have moved each of the four technologies toward meeting the $2/kg goal. Furthermore, it is difficult to put in perspective where each of the four technologies stands relative to meeting the $2/kg goal. While it is not necessarily a weakness, it would be beneficial to understand how the funding is allocated among the four water-splitting technologies, with which of the four technologies the nodes being utilized align, from which technology data is being accessed, etc. This understand would provide a better understanding of how the capabilities, expertise, and R&D for each technology is being utilized.
- HydroGEN's strength is also a weakness. The communication within HydroGEN is extremely positive, but having so many partners involved takes a good deal of time and resources that could be used for achieving the project's goals. However, the question is whether communication is not the better way to accelerate the process.
- It is not clear how to directly assess the impact of the consortium as a whole on progress toward DOE targets. This is admittedly a challenging problem. While the individual projects themselves have clearly defined go/no-go decision points and can point to performance metrics and demonstrations, assessment of the consortium and its contributions in tandem is much more challenging. It may be beneficial to consider ways of showing evidence of the impacts of the nodes themselves on the success of HydroGEN activities.
- The project's weaknesses include that it is covering a broad range of R&D areas and fields, which presents a communication challenge and brings into question whether scientists can speak the same "language." Other weaknesses include how the project team will break down the main goal of $2/kg of hydrogen into subtargets for different R&D tasks for materials development, as well as internal competition.
- An overview of measurable progress in each technology was not provided. Go/no-go milestones appear to be missing from the presentation.

Recommendations for additions/deletions to project scope:

- The project scope is just right, given that HydroGEN's goals are focused on materials. If the market introduction of clean hydrogen were the goal, much more effort on engineering topics and product development would be necessary.
- As HydroGEN moves toward its renewal, a "deep-dive" technical evaluation of each of the four water-splitting technologies being pursued should be considered. The evaluation would help in understanding where each of the four technologies stands toward meeting the DOE target relative to the other three technologies, what the major challenges are that need to be addressed, and what the likelihood is of

addressing those challenges, with the purpose of best deciding how to allocate funding and resources. While it is understood that DOE does not pick winners, and picking a winner is not necessarily being advocated, how to best allocate limited funding is a critical issue.

- The project team should find a way to quantify progress of all parallel efforts and associate timeline and TRL with it.

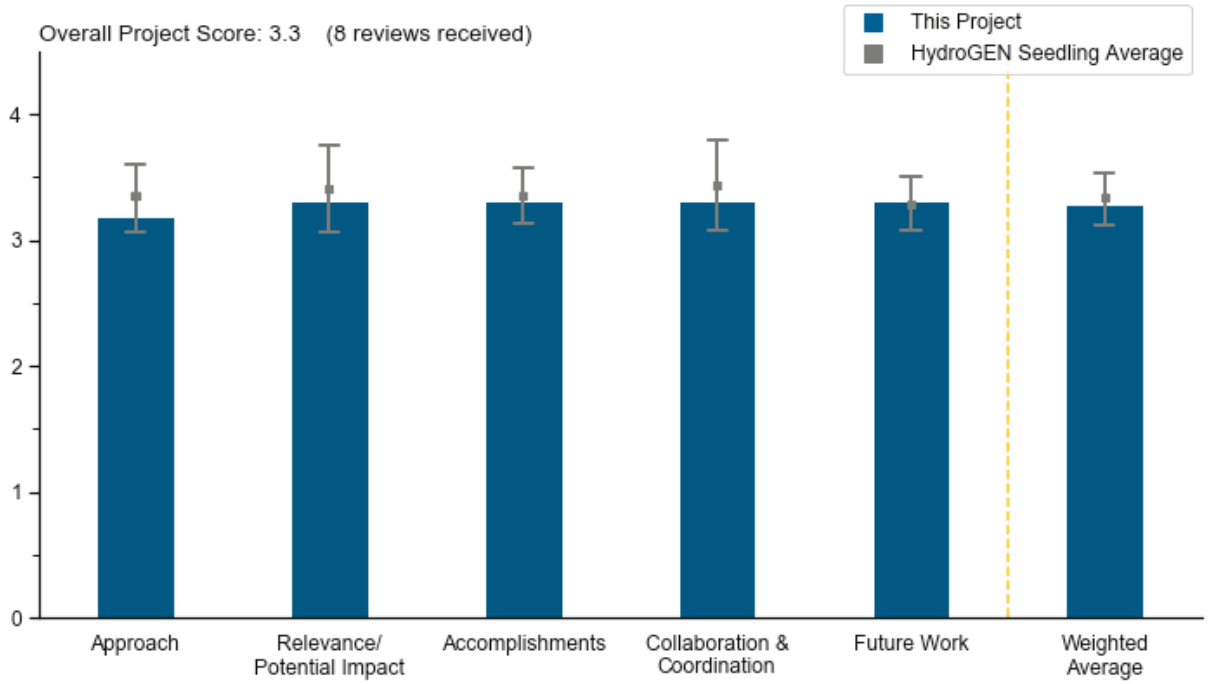
Project #P-152: Proton-Conducting Solid Oxide Electrolysis Cells for Large-Scale Hydrogen Production at Intermediate Temperatures

Prabhakar Singh, University of Connecticut

Brief Summary of Project

The primary objective of this project is to identify novel materials and processing techniques to develop cost-effective and efficient proton-conducting solid oxide electrolysis cells (H-SOECs) for large-scale hydrogen production at intermediate temperatures (600°C–800°C). New proton-conducting electrolytes, tailored hydrogen and oxygen electrodes, and optimized cell designs for lowering the electrode polarization and resistive losses will be developed. Following synthesis and characterization of new electrolyte and electrode materials, they will be used for the fabrication of solid oxide electrolysis cells (SOECs) and tested for performance and durability. The project will examine degradation mechanisms and optimize materials chemistry and component structures to mitigate any degradation.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.2** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- This is primarily a materials development effort aimed at the "BZCY-Yb" proton-conducting ceramic electrolyte material, which has some interesting attributes for high-temperature electrolysis systems. The team is pursuing a sol–gel approach for BZCY-Yb powder preparation, which has shown promise in reducing sintering temperature. Reducing the sintering temperature is essential for designing a practical cell fabrication process. Without details on the sol–gel process being used, it is difficult to assess the cost-effectiveness.

- In general, the project's research approaches are excellent. It would be good if there were clearer motivation for lowering sintering temperature below 1400°C and using the sol–gel method to prepare powder.
- The approach focuses on non-noble, non-Pt, low-cost materials and scalable processing. Emphasis is placed on low-temperature processing (i.e., targeting low-temperature kilns that use cheaper Kanthal elements, ~1300°C and below), while preserving the bulk, interfacial, and surface properties required for electrolyzer operation. The interaction between fluorite and perovskite materials was also probed.
- The approaches to address the identified technical barriers are logical and reasonable.
- This project has a comprehensive approach.
- This is a sound approach; however, the uniqueness of the project is not completely clear.
- The project team is advised to review the instructions of creating Hydrogen and Fuel Cells Program (the Program) Annual Merit Review slides carefully. The instructions advise listing the technical barriers being addressed, as described in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRDDP). The authors have not identified these barriers in accordance with the MYRDDP. The approach to improving the material performance and fabrication seems sound, but it is unclear how some of the work will affect the barriers in question. It would be beneficial to understand which barriers were being addressed by various tasks.
- The oral presentation and presentation materials do not give a good sense that the project is grounded in solving one or two key problems. There seem to be multiple moving parts to this project, and it is not apparent how they mesh.

Question 2: Relevance/potential impact

This project was rated **3.3** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The focus of this project is on industrially relevant parameters rather than on record-setting (but short-term and unstable) performance. The processing focus should prove useful for assessing the feasibility of manufacturing SOEC stacks using conventional, scalable technology in optimal ways. The emphasis on lowering the processing temperature is one of the project's unglamorous but very useful efforts, since typical SOEC materials like Zr are highly refractory but also contain volatile elements, such as Ba, that evaporate and have deleterious effects on the defect chemistry of the vital components. It also should be cheaper to process at lower temperatures, if the dwell times are also reasonable.
- Solid oxide electrolysis is a key component of the DOE's emerging portfolio of hydrogen production technologies. If this project is successful, a new materials set will be available for designing solid oxide electrolyzer systems. Thus, this project has relevance and a significant potential impact. The challenge will be to take the materials technology developed on this project to the full-scale stack level and, ultimately, to large-scale system levels.
- In general, the project has significant potential to meet DOE goals. The synthesis and fabrication processes based on the sol–gel method and infiltration should be justified for large-scale production, and the cost estimation should be reasonably included in the future technoeconomic analysis (TEA).
- The impact of this project is quite clear and beneficial to H-SOEC systems. It would be beneficial to see the impact of the new materials, not just under electrical testing but under a hydrogen production test as well.
- The project is relevant to high-temperature water electrolysis.
- The impact and relevance are clearly seen. There are no issues to raise.
- The project aligns well with the Program.
- It is not apparent that the project is addressing a critical path issue for steam electrolysis. Lowering the sintering temperature sounds useful, but it is not clear that this is one of the top hurdles for the success of the technology. However, the project does seem to be engaged and contributing to the HydroGEN network.

Question 3: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project is pursuing solutions to one of the major challenges that has limited the potential of high-temperature proton-conducting ceramics, specifically the need for excessively high temperatures for densification. The team has made good progress on this. They also have demonstrated high proton conductivities in their low-temperature sintered materials.
- The project achieved significant progress within one year by showing promising current density and lower sintering temperature. In general, the project's accomplishments are outstanding.
- The project is proceeding as proposed. Excellent progress has been made with respect to current density and electrolyte thickness.
- The project has made excellent progress toward its overall goals.
- The project goals are on track; however, it seems like little progress was shown in the presentation as compared to the review from the previous year. Other aspects should be evaluated, such as the effects of Cr poisoning on durability. The 3% H_2O during testing seems rather low.
- The project has met Phase 1 milestones. It would be helpful if the principal investigator (PI) would clarify that the cells being tested were prepared using the lower-temperature sintering approach.
- The project team has achieved budget period (BP) 1 milestones. The use of ZnO as a sintering aid has been covered by Liu's group before (see citation below) and others in the past, and there is a great deal of work that can be found in literature on sintering aids and less refractory dopants for BZY. The combinatorial sintering aid study in BP 2 needs to work harder to advance sintering aid knowledge, beyond what is already known. (Wenping Sun, Zhen Shi, Mingfei Liu, Lei Bi, and Wei Liu. "An Easily Sintered, Chemically Stable, Barium Zirconate-Based Proton Conductor for High-Performance Proton-Conducting Solid Oxide Fuel Cells." *Advanced Functional Materials* 24, no. 36 (2014): 5695-5702. doi:10.1002/adfm.201401478.)
- The accomplishments of this project do not seem overly significant, considering the primary objective of the project is to create H-SOEC electrolyte materials at low temperatures and to provide lower-cost hydrogen production capability. First, the temperature reduction from 1450°C to 1350°C is small. Most industrial equipment that operates at 1350°C can also operate at 1450°C, suggesting that there would be little material cost savings in production equipment. The operating costs to go from 1350°C to 1450°C would be insignificant to industrial equipment that can operate at temperatures greater than 1000°C. If there are cost savings to be found, they should be addressed directly. Secondly, while the authors are commended for performing a durability test, 50 hours is extremely short. It would beneficial to show the test data and let it run to failure. Finally, the authors should consider showing the performance of the current state of the art on many of their metrics. It would be beneficial to show the audience how large the improvements being made to the state of the art are or how close the new technology has come to providing a function similar to the state of the art.

Question 4: Collaboration effectiveness

This project was rated **3.3** for its collaboration and coordination with HydroGEN and other research entities.

- These two organizations (the University of Connecticut [UConn] and Pacific Northwest National Laboratory [PNNL]) have been at the forefront of solid oxide fuel cell technology for many years. It is good to see these two powerhouses collaborating on a project such as this one. DOE is also commended for setting up the H2@Scale program to facilitate collaborations between project teams and national laboratory nodes funded under the HydroGEN program. This enables many resources to be brought to bear on addressing challenging technical issues.
- This appears to be a well-integrated effort, with UConn, Idaho National Laboratory (INL), National Renewable Energy Laboratory (NREL), and PNNL all contributing. However, the PI could do a better job of articulating the roles and responsibilities of the different organizations. For example, it is not entirely clear what the UConn researchers have contributed.

- In general, the collaboration between the team, institution, and Energy Materials Network (EMN) nodes is excellent. If the connection between the NREL's screening and the validation of the material can be further improved, it would be better.
- There are several collaborators involved in this project. The EMN is being leveraged, NREL will do combinatorial work on sintering aids, and INL is performing the cell testing. However, no direct references were made to how the project is leveraging or contributing to the HydroGEN Data Hub.
- The project's collaboration and coordination are adequate and as proposed.
- The interactions between collaborators are appropriate.
- No issues were identified with the project's collaboration.
- It is unclear how the modeling effort at Sandia National Laboratories is being used to support the project's experimental work.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- A very useful focus included in the future work will be to analyze and present the contributions for each conducting species in order to assess whether a useful transference number is attainable, especially with the lower firing compositions where sintering aids could create unwanted electronic defects.
- The proposed future work is a logical continuation of the presented effort. Thermal cycling should be part of future testing.
- This project appears to be on track, and future work is aimed at addressing the project's remaining milestones.
- The project team should just keep up the momentum. They are doing good work.
- The proposed future work is excellent. It would be better if the team could show a stronger connection between the theoretical and experimental work.
- The PI did not have time to convey plans for future work during the presentation, so the following comments are based off of the presentation materials. Generally, the Phase II plan seems sound. It is questionable that the team will be able to "demonstrate...cost of H_2 production <$2/gge" by quarter 12, as listed under (e) on the "Proposed Future Work" slide.
- More details should be given on the proposed approaches for future work.

Project strengths:

- The project has integrated multiple efforts into one and has achieved an outstanding current density. The proposed roll-to-roll fabrication of cells and stacks is very interesting. It would be good if the team could include the new innovative synthesis and fabrication in TEA.
- The project's strengths include the technical prowess of the team, the powder synthesis technology that is being applied to reduce the sintering temperature of the electrolyte material, and the fabrication process that is being used to fabricate cells.
- The project's strengths include the quality of the team. This is a good technology area on which to work (e.g., steam electrolysis, proton-conducting electrolyte).
- The project's strengths include the large network it has to work within. The electrical results seem encouraging, the new synthesis operations seem to be producing good cells, and the project is meeting technical targets.
- The project has a reliance on and is using the strengths of its collaborators. Excellent progress has been made with respect to optimizing electrochemical performance.
- The project's main strength is in the approaches that have been taken to address the critical technical issues to date.
- The emphasis is on industrially relevant parameters. The project team has achieved the BP 1 milestones.
- The project is incrementally improving SOEC performance.

Project weaknesses:

- The actual hydrogen generation rates need to be measured. This will be done as part of the transference number calculations in BP 2, but it is vital to the meaningful interpretation of the I–V curves for the tested cells that have been presented. There remains room for innovation in the approaches to decreasing the processing temperature and maintaining performance of the cells. Judging by the apparent cell shrinkage during firing, the fabrication of cells with 25 cm^2 of active area will be extremely challenging.
- The presentation needs improvement. The presenter used up most of his time before reaching slide 6. This limits the time available to view and understand the technical data. Despite being a major project goal, no information was reported on cost reduction—or even notional cost reduction for future cases. It is also unclear from the presentation how some technical barriers are being addressed.
- The project's weaknesses include the clarity of the presentation and the project's time management. The project team needs to articulate why specific project objectives are on the critical path for steam electrolysis, as well as what the size of the prize is.
- The targets for performance and stability may have been set too conservatively. The milestones have been met with ease. It may be possible to be more aggressive going forward.
- The endpoint of the project is the testing of a three-cell stack; there will be a long way to go after the project is completed.
- The team needs to better demonstrate the uniqueness of the project.

Recommendations for additions/deletions to project scope:

- The project team should be sure to probe the transference numbers and ensure that the materials are in equilibrium when doing so. This is not trivial but vital to getting useful data about the materials. There are some conflicting data in the field at the moment.
- Materials modeling is recommended to help guide and explain experimental results, which would better enable future research and development to build off the results of this effort.
- A small effort is recommended to determine the mechanical properties (e.g., fracture toughness) of the electrolyte.
- If time allows, the project team should increase stability test duration.
- Test conditions and characterization parameters are missing on most figures. No changes to the project scope are suggested.

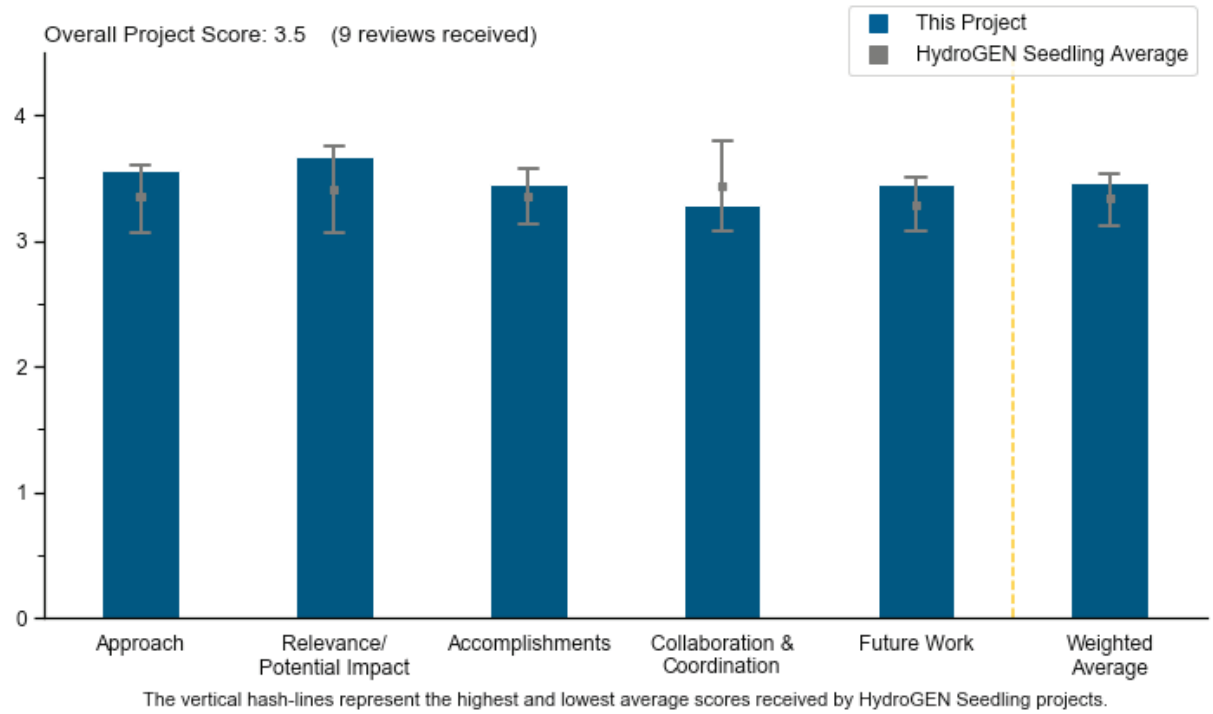
Project #P-153: Degradation Characterization and Modeling of a New Solid Oxide Electrolysis Cell Utilizing Accelerated Life Testing

Scott Barnett, Northwestern University

Brief Summary of Project

Solid oxide electrolysis cells (SOECs) have the potential for high electricity-to-hydrogen conversion efficiency, but these cells lack long-term stability, particularly at high current density, and the degradation mechanisms in SOECs are poorly understood. The project aims to develop mechanistic degradation models that realistically predict long-term SOEC durability, using input data from accelerated electrochemical life testing combined with quantitative microstructural and microchemical evaluation. Also, a promising SOEC cell type with high performance will be further developed. The understanding achieved by combining experimental results and theory will be used to guide improvements in long-term SOEC durability.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.6** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The approach of this project brings much-needed fundamental analysis to SOECs to help explain a common electromechanical failure mode of the cells. Testing and theory are coupled in this work, allowing for far-reaching results that could enable insights into other material sets as well.
- This project is aimed at understanding and addressing degradation in SOEC electrodes, which will be essential for the successful development and deployment of high-temperature electrolyzers. The project approach includes an appropriate balance of theory, new materials development, and long-term durability testing.
- The project has a clearly defined research objective, which is the quantitative prediction of SOEC durability, and a plan to combine experiments and modeling to get there.

- The approach is outstanding, which is enough to perform the proposed work and fulfill the milestones and the U.S. Department of Energy's goals.
- There is excellent incorporation of theory and modeling from the Energy Materials Network resources.
- The approach seemed reasonable. The use of experimental data to validate the models is important.
- The approaches are reasonable and logical.
- The approach to this work seems sound. The modeling efforts support the hypothesis that overpotential is related to failure. A comprehensive set of materials is being tested. However, the current densities selected for study are seemingly out of place. To begin with, the approach slide suggests that the state-of-the-art current density is at 0.5 A/cm^2, yet solid oxide tests are often run at 1 A/cm^2. Some companies have reported that they could run above this current density, but they do not find it to be advantageous to do so. Failure studies were conducted at only 0.8 A/cm^2 and 1.6 A/cm^2. Studies should be presented at some midpoint current density as well.
- The approach is clear; however, it seems to be lacking other degradation mechanisms that could affect the model.

Question 2: Relevance/potential impact

This project was rated **3.7** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- Solid oxide electrolysis is a key component of DOE's emerging portfolio of hydrogen production technologies. Understanding cell degradation modes under the unique conditions intrinsic to solid oxide electrolysis (e.g., high steam contents on fuel electrodes and high overpotentials on air electrodes) will be critical for the successful development and deployment of large-scale solid oxide electrolysis systems. Thus, this project has high relevance and significant potential impact.
- The work is highly relevant to SOEC development because it combines experimental work with fundamental defect chemistry and the mechanics of the materials. The critical findings can educate other material sets used for SOECs—and likely for other devices as well. Calculating a critical overpotential for degradation that is informed by oxygen pressure and material strength should have far-reaching impacts, as it is relevant to more than just this set of materials.
- Solid oxide electrolyzer degradation is a key challenge to SOECs. It is important to understand the degradation mechanism in order to develop new materials and cell designs that can mitigate the degradation. The degradation models being developed here can be integrated into the cell, stack, and system models for better projection of stack performance.
- The highest-efficiency electrolysis approach is very relevant. The project is demonstrating substantial progress toward SOECs with long lifetimes.
- The project is highly needed for the prediction of long-term stability, which directly answers long-term stability goals.
- The project is relevant to high-temperature water electrolysis, addressing one of the failure mechanisms in SOECs.
- The project is focused on a critical path issue for steam electrolysis: durability.
- The project aligns well with the DOE Hydrogen and Fuel Cells Program.
- The work is directly relevant to improving solid oxide electrolysis projects; however, it seems that the expected operating conditions for such projects are not in line with the tested conditions presented here.

Question 3: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project's accomplishments include the correlation of testing conditions (e.g., current density) with degradation rates and cell failure, stable cell operation at 1 A/cm^2 with the novel $Sr(Ti_{0.3}Fe_{0.7-x}Co_x)O_{3-\delta}$ (STFC) air electrode for 1,000 hours, and agreement between the model predictions and observed failures at the air–electrode/electrolyte interface.

- The elucidation of oxygen potential and fracture conditions is very important. It would be good to see the team include outside data in the analysis and make connections to groups that could provide more robust values for key physical properties, such as the fracture toughness of novel materials involved in the SOEC formulations.
- The project team has successfully completed the budget period 1 milestones. The project has demonstrated theoretical work that matches observed experimental failures and conveniently correlates with the available strength data for materials.
- The project has achieved outstanding progress and is on the perfect track to meet its milestones.
- The work is progressing as proposed and exceeding expectations year to year (the proposal was ambitious).
- The project goals are on track, with good progress made during the last year.
- The authors are making excellent strides toward achieving their goals. The go/no-go decision seems somewhat unclear. It is not clear whether they are aiming to predict cell degradation to within 30% accuracy or to improve degradation rates by a similar factor.
- The integration of a reference electrode was well done. This will be key in understanding the failure mechanisms. The identification that failure occurs when the overpotential is above 200 mV is important. It is unclear whether failure for this material set starting at overpotentials above 200 mV can be extrapolated to other material sets and other temperatures. Slide 11 says the voltage degradation is flattening out; however, the data do not support this assertion. It clearly looks like the voltage is continuing to degrade. The researchers should have continued the test. The modeling work examining the effect of operating conditions assumes a uniform current density across the cell. However, the current density will vary depending on the position in the cell. The model needs to account for the varying current density. It is well known that high current densities and high steam contribute to the degradation. This work is starting to quantify the levels at which cracking and damage occurs.
- It is not clear once the degradation is identified what the path forward is to prevent it; it could be material selection, careful selection of operating conditions, etc. It would also be beneficial to know how the cost of hydrogen will be affected, following the model's suggestions. Other aspects such as Cr poisoning effects on durability, processing parameters, and thermal cycling should be considered.
- The information presented does not convincingly demonstrate that overpotential or current density is the only root cause for cracks experimentally observed in the electrolyte that is formed experimentally by sintering. For example, other considerations may include defects in the electrolyte; defects in the sintered electrolyte could cause cracking under high current flow.

Question 4: Collaboration effectiveness

This project was rated **3.3** for its collaboration and coordination with HydroGEN and other research entities.

- The metal-supported SOEC testing at Lawrence Berkeley National Laboratory (LBNL) is an interesting start in the use of that cell structure. It will be insightful to see where the limitations and improvements of that approach will be. Cell testing at Idaho National Laboratory (INL) provides experimental data to educate the modeling work, in addition to the testing at Northwestern University (NU). This provides a third-party dataset that should help strengthen the signal of useful correlations and dampen noise of the contributions of confounding variables that are operator- or facility-related. The team specifically mentions utilizing and providing information for the Data Hub.
- This is a good start to engaging with the HydroGEN nodes and is set to grow. The project team is strongly encouraged to make plans to share and obtain datasets via the Data Hub. The team should be actively seeking datasets to further test and validate modeling.
- While the HydroGEN team seems well utilized, the authors may wish to reach out to industry experts to confirm their capabilities and operating conditions.
- The collaboration with the national laboratories is outstanding. It would be better if collaboration with other universities could be included.
- The interactions between collaborators are reasonable.
- No issues are observed; collaboration is proceeding as expected.
- The team members are fairly well coordinated.
- Communication with the benchmarking project is very important. The research team needs to get additional degradation data to compare the project theory with work done by others. INL has extensive data, so it was

surprising not to see this mentioned in the data used in the project. Considerable degradation modeling has been done by the Solid State Energy Conversion Alliance (SECA) for solid oxide fuel cells (SOFCs). While some conditions are different, there is some knowledge that could be gained from discussions with SECA participants at the National Energy Technology Laboratory (NETL), Pacific Northwest National Laboratory (PNNL), and West Virginia University, who have been doing modeling of SOFCs. NU is encouraged to reach out to them and see if there is possible collaboration or work that can be leveraged.
- It is not clear that there is much coordination between the work being done at NU and the work being performed by LBNL and INL.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The proposed future work for fulfilling the milestones is outstanding. If the starting work for a new protonic ceramic electrolyzer system is initialized, it would be fantastic.
- The proposed future work is a logical continuation of the presented effort. Thermal cycling should be part of future testing and considered in the model.
- Continuing to study the correlation of critical overpotentials with lifetimes will be useful, especially for the different cell types.
- The researchers are looking to continue validating their models and expanding the materials set tested, which is excellent.
- The proposed future work seems well thought out and will provide excellent progress for this project.
- This is a very good use of DOE funds.
- The future work is commensurate with the stated objectives of the project.
- Reasonable future work is proposed.
- The proposed future work is logical, but more details should be given, especially regarding the approaches.

Project strengths:

- This project effectively combines theory and experimental results in an impressive fashion. The strength of the correlation between interface overpotential and mechanical failure has intuitive appeal from a fundamentals point of view, and it appears to be born out of a meaningful quantity of experimental data.
- The project provides a unique and effective methodology for predicting long-term stability based on the optimization of operating conditions and materials selection, etc. The success of this project will help the commercialization of high-temperature electrolysis significantly.
- The project is focusing on a critical issue for steam electrolysis. The team has a clear hypothesis and plans to test it, and team members are utilizing both modeling and experiments.
- The project's strengths include its focus on degradation and its novel electrode materials, which are showing promise.
- The project team is using a good combination of experiment, characterization, and theory to develop the degradation models. The researchers have a solid background in this area.
- There is good focus on a critical subject. This is a strong team, with good research expertise and seemingly strong modeling and predictive capabilities.
- The main strength of the project is the complementary expertise of the team (including NU, INL, and LBNL).
- The project is identifying operating conditions in which cell failure can occur.
- The model is providing reasonable predictions, even without fitting parameters.

Project weaknesses:

- There are no obvious project weaknesses yet.
- The project team needs to ascertain whether the very simplified Butler–Volmer approach is appropriate for all the situations that have been considered. The team needs to determine what is causing the steam variability during long-term testing. The cycling can be deleterious to the cells and could be a confounding variable that is not adequately controlled.

- The researchers are using a limited set of materials. They should reach out to INL and SECA, who have additional data that may be useful. The models have some assumptions that need to be adjusted. For example, they are assuming constant current density across the cell. This is a poor assumption. There are additional SOEC models that can describe how current changes, which could be used to give better results. PNNL and NETL have models that can do this for SOECs.
- The project team needs to confirm operating conditions for current density. It is suggested that the project do a wider range of failure tests at different current densities and reach out to industry for review and input.
- The project team is not getting as much out of HydroGEN as it probably could.
- The model seems to target only one degradation mechanism.

Recommendations for additions/deletions to project scope:

- If the initial study on proton-conducting SOECs were added, the scope would be fantastic.
- The project team should consider including additional elements in the model, e.g., fuel effects and current density gradient. The project should verify that, as the model gets more detailed, it does not turn out that the early promising results were just fortuitous.
- The project team should relate these degradation processes to their effect on limiting the efficiency of SOEC operation under different conditions (e.g., temperature and reactant flows).
- Test conditions and characterization parameters are missing on most figures.

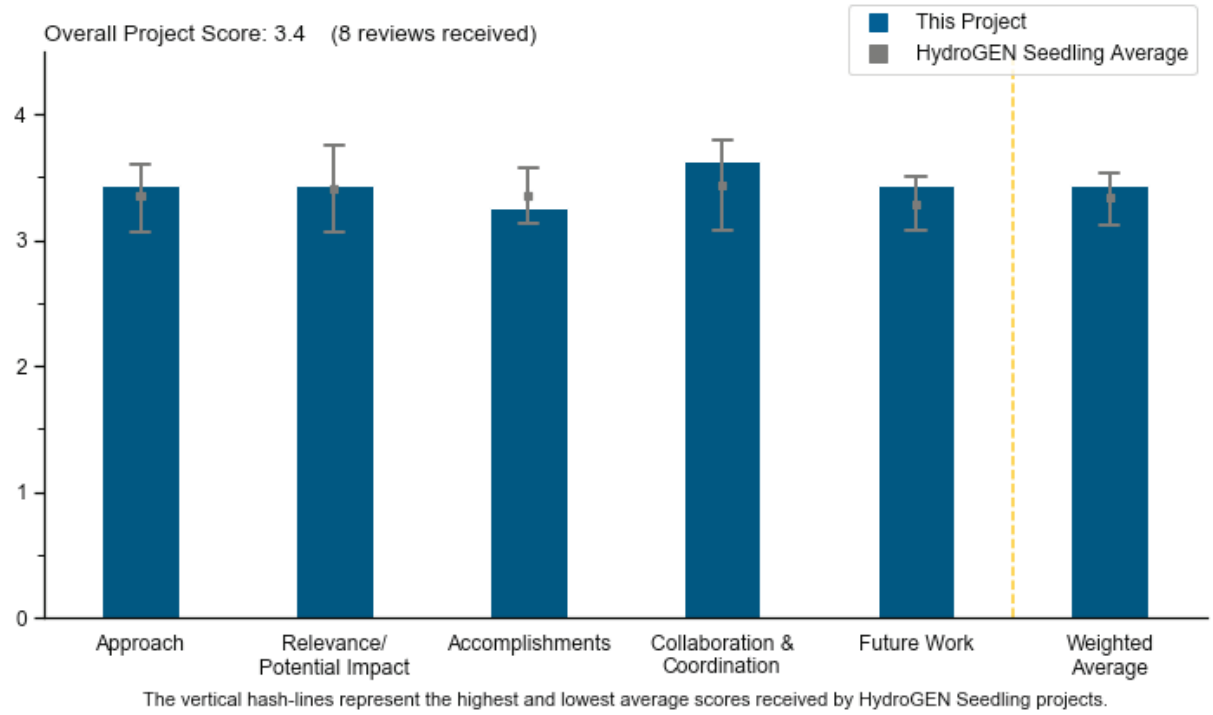
Project #P-154: Thin-Film, Metal-Supported High-Performance and Durable Proton–Solid Oxide Electrolyzer Cell

Tianli Zhu, United Technologies Research Center

Brief Summary of Project

This project is developing a thin-film, durable, metal-supported solid oxide electrolysis cell (SOEC) using a proton-conducting electrolyte at targeted operating temperatures of 550°C–650°C. This advanced SOEC will provide a highly efficient, cost-competitive high-temperature electrolysis process for hydrogen production. Initial efforts focus on demonstrating the feasibility of the proposed concept by further advancing metal-supported single cells based on work completed previously for solid oxide fuel cell (SOFC) applications. Cell fabrication, especially electrolyte deposition via suspension plasma spray (SPS) processes, is a focus.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.4** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The project has a reasonably comprehensive strategy to develop a lower-cost fabrication approach to proton-conducting SOECs (P-SOECs), building off of previous SOFC experience. The approach is integrating fabrication, characterization, testing, and modeling.
- The project has a viable approach, low-cost production and assembly, and an opportunity for a high-durability system.
- The project's approaches to addressing the identified technical barriers are logical and appropriate.
- Plasma spray for proton-conducting membranes may solve several of the manufacturing challenges that are associated with this technology. By operating at temperatures less than 700°C, the team may be able to use lower-cost materials and have lower degradation.
- In general, the proposed approaches are excellent. If the project adds an approach to further improve SPS fabrication of the dense electrolyte and the porous electrode, it will be better.

- There are some compelling reasons to consider proton-conducting ceramic electrolytes for electrochemical water splitting to produce hydrogen. The temperatures are high enough that precious metals are not required in the electrodes, yet not so high that thermal integration is challenging. The ionic conductivity of proton-conducting ceramic electrolytes at 600°C can be similar to that of oxygen-ion-conducting ceramic electrolytes at 800°C. The metal-supported, thin-film electrolyte SOEC architecture that is targeted in this project makes a lot of sense for minimizing resistance (and power consumption) during electrolysis. A significant challenge is that barium-zirconate-based proton-conducting ceramics require very high sintering temperatures for densification, which makes it difficult to achieve high-density electrolyte architectures. The approach being pursued in this project is even more challenging because the barium-zirconate electrolyte coatings need to be sintered under conditions that are compatible with the porous metal support. There is a concern that it will be extremely difficult to achieve sufficiently high electrolyte density while simultaneously achieving proper morphologies of the metal support and fuel electrodes. Another challenge is that it is not easy to design electrochemically active and stable electrode materials for operation at 600°C.
- The overall approach is very complete and promising; however, the plasma spray might be a risky technique to control all parameters.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- Solid oxide electrolysis is a key component of DOE's emerging portfolio of hydrogen production technologies. If this project is successful, a promising metal-supported cell technology will be available for subsequent development of stack technology and ultimately large-scale solid oxide electrolyzer systems. Therefore, this project has relevance and a significant potential impact.
- Materials development for water splitting is relevant to DOE work. The state of the art for SOEC performance seems low compared to what is in other presentations. There are several groups achieving >1 A/cm^2 at <1.4 V and 800°C. The target of 4 mV/1000 hours seems reasonable. If cells can be manufactured at the projected cost in low volume, this will accelerate SOEC commercialization.
- The achievement of the project objectives can align well with the DOE target for long-term, low-cost, and efficient high-temperature electrolysis. The metal-supported P-SOEC represents one of the most promising research efforts among SOECs.
- This project relates very well to the goals of improving solid oxide performance as it pertains to DOE targets. The authors have also included a suggested cost analysis for hydrogen produced from the proposed system. The low costs do seem highly dependent on the electrical cost being $0.04/kWh, which is very low for electrical costs.
- The project is relevant to high-temperature water electrolysis that uses an alternative to traditional fabrication processes.
- The performance, durability, and stated costs indicate the potential for a viable electrolysis system.
- The project aligns well with the DOE Hydrogen and Fuel Cells Program.
- It is not clear that manufacturing cost is one of the top barriers to SOECs. It would be beneficial to see a stronger connection to durability. However, the team is clearly leveraging and contributing to the HydroGEN Consortium.

Question 3: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- There are substantial and meaningful results across the different research thrusts. The project has not been all smooth sailing, which usually means the team is working on the important parts.
- The project has made excellent progress.
- The project goals are on track, with good progress made during the last year. It is not clear how far the present system is from the assumed conditions for hydrogen cost. The team needs to consider what needs to

be achieved to reach a $1.35/kg cost target for hydrogen. The project takes a holistic approach in addressing different aspects for cell fabrication. Thermal cycling should be a part of the stability testing.

- Thus far, the results are promising and meet the Phase I targets. However, it is noted that the steam concentration required to achieve some of these targets is very low, less than 20% H_2O. Ideally, this concentration would be higher for large-scale operating.
- This project has made progress, but it looks like the issues to be addressed are quite challenging.
- The project fulfilled its go/no-go milestone. The electrolyte property can be further improved.
- The 3% steam content for some of the tests seems very low and does not represent what a real system would experience. It would be helpful if the presentation included the flow rate and steam utilization. If the project is using a high flow rate and low utilization, the steam content may not be a problem. However, a high flow rate and low utilization may skew the performance, making it look better than it actually is. The data indicate that as the steam content was decreased, the performance increased. This was surprising since the reverse is true in most of the literature. The researchers should explore this result, as it could have significant impact on the operation of the stack. The use of a metal support limits how high the sintering temperature can be. Therefore, it is not surprising that defects in the electrolyte are apparent, since a low sintering temperature is being used.
- Although the Phase I go/no-go milestone and performance target was met, the density of the SPS-processed electrolyte is not sufficient and contains unreacted $BaCO_3$. Also, the performance target was met with a fuel-electrode-supported cell rather than a metal-supported cell.

Question 4: Collaboration effectiveness

This project was rated **3.6** for its collaboration and coordination with HydroGEN and other research entities.

- This project has a strong team involving an extremely qualified consultant, the University of Connecticut, as a subcontractor and several HydroGEN national laboratory nodes. The ultimate SOEC technology that is being developed will require contributions from all of these team members.
- This project is one of the best examples of a team engaging multiple HydroGEN nodes to make key contributions to the project.
- The collaboration appears vibrant and effective. No issues are apparent.
- The project team seems well suited, and work seems to be progressing fluidly.
- There are good interactions occurring with the nodes.
- The team has outstanding collaborations. If the electrochemical modeling information can be used as guidance for other processes, it will be better.
- The coordination between the team members has been effective, but closer coordination may be needed between the fabrication and material development team members.
- The collaboration seems to be well organized. The project is using the HydroGEN nodes well. Pacific Northwest National Laboratory and Boston University are listed as collaborators, but they are not on the project. The team should clarify how those institutions are contributing.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The future work seems to cover all the steps necessary to improve this technology.
- The proposed future work is consistent with the project objectives. The major focus should be on increasing electrolyte density and achieving the performance target on a metal-supported cell.
- The focus is on production optimization and durability testing. This is where effort should be spent. More cost information is desired; this is in large part as a result of the very enticing cost numbers that were reported. To be candid, the SPS process seems almost too inexpensive. Future work should indicate the assumptions related to the process scale used to estimate cell and stack production costs.
- In general, the proposed future work is excellent. If the team can improve the clarity for targeting the remaining challenges, it will be better.

- The proposed future work is a logical continuation of the presented effort. Thermal cycling should be a part of future testing.
- The proposed future work is appropriate; however, some details on the proposed approaches are needed.
- It is hard to judge the proposed future work based on the brief outline in the presentation materials. It would be helpful to see a milestones chart for the current phase.
- The use of a metal support limits the sintering temperature, resulting in defects in the electrodes. The researchers do not give a strategy for how they will develop a dense electrode layer without the high-temperature sintering required. The future work focuses on the issues of electrode densification and durability. It would be good to see the details of the cost analysis.

Project strengths:

- The project's strengths include its collaborations and its leveraging of the HydroGEN nodes. The team has a strong research plan and is working on valuable objectives (e.g., steam electrolysis, P-SOECs).
- The project has a very strong, collaborative team, and the approach of metal-supported, thin-film P-SOECs is unique. SPS fabrication is promising and may be cost-effective.
- The project's strengths include the development of a unique fabrication technique that can lower fabrication costs.
- The project is well organized, with excellent results to start. The team included a cost analysis with promising results.
- This is a strong team. Plasma deposition is an interesting approach. The project is using the HydroGEN nodes well.
- The project's main strength is in the approaches being conducted to address the technical barriers.
- The project has the potential for a viable system that meets DOE targets.
- This is a strong team. There is a potential for lowered costs.

Project weaknesses:

- The project has no major project weaknesses, although it appears that the issues are quite challenging, considering the level of effort.
- The team may need to consider further processing steps or different fabrication techniques if sufficient densification is not achieved.
- The team should consider the cost of electricity for analysis. The team needs to explain or increase the steam concentration for the feed.
- The researchers need to test their cells with more realistic steam levels and steam utilization. They are using a metal support with materials that require high-temperature sintering. This will be very difficult to solve.
- There is a focus on fabrication versus durability.
- The cost estimations appear too optimistic. Greater detail should be reported.
- There is extreme technical difficulty associated with achieving project success.

Recommendations for additions/deletions to project scope:

- The team needs to focus on achieving high electrolyte density in the final metal-supported platform.
- There should be an increased level of detail regarding cost estimation.
- No additions or deletions are suggested.

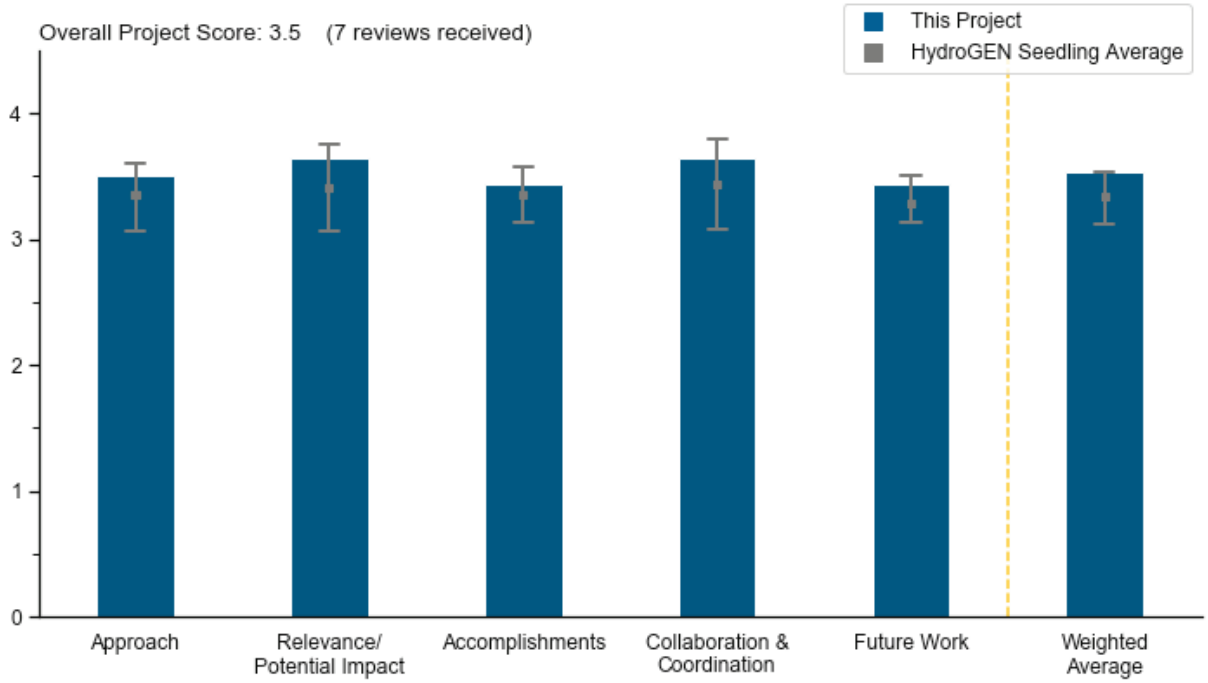
Project #P-155: High-Efficiency Polymer Electrolyte Membrane Water Electrolysis Enabled by Advanced Catalysts, Membranes, and Processes

Kathy Ayers, Proton OnSite

Brief Summary of Project

This project will develop an advanced, highly efficient polymer electrolyte membrane water electrolysis (PEMWE) membrane electrode assembly (MEA) by addressing membrane, catalyst, catalyst layers, and their interfaces. Four areas affecting cost and efficiency will be developed: (1) thinner membranes, (2) lower catalyst loadings, (3) optimized gas diffusion layer and porous transport layer materials and structures, and (4) increased operating temperature. Successful demonstration and integration of these four areas require a deeper understanding of the scientific and technical aspects of PEMWE MEAs. Proton Onsite will partner with University of California, Irvine, and Oak Ridge National Laboratory (ORNL)—with support from the National Renewable Energy Laboratory (NREL) and Lawrence Berkeley National Laboratory (LBNL)—to integrate advanced cell designs and materials and fundamentally characterize performance.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.5** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The general approach of this project is to improve catalyst materials, reduce membrane thickness, and increase operational temperature. This is very reasonable for achieving better electrolyzer efficiency and lowering the cost of hydrogen production. Based on results obtained previously, the team is continuing studies on durability, membrane material hydration and down-selection, the electrode preparation process, and advanced characterizations. These are all appropriate for reaching the project's final goals.
- Thinner membranes and alternative catalysts have shown promise for the stable operation of polymer electrolyte membrane (PEM) electrolyzers with improved efficiency. This project advances material performance and integrates components, while leveraging fundamental characterization to understand and

push design limits. The project is taking a multifaceted approach to understand the effect of catalyst, electrode, and membrane performance on overall cell performance. The issues that need to be addressed are identifying active and durable membranes with thicknesses below 50 microns, reducing the catalyst loading by a factor of 10 while avoiding catalyst dissolution at low loading, synthesizing and integrating higher-activity oxygen evolution reaction (OER) catalysts into the anode, understanding how the electrode and substrate porosity affects performance, refining the cell architecture, and completing the imaging and characterization of the electrode after operation. The goal is to reduce catalyst loading by a factor of approximately 10 and achieve hydrogen production at or below $2/kg.

- PEM electrolyzers are still based on rudimentary catalyst-coated membrane concepts, with thick membranes, high catalyst loadings, and platinum-group-metal (PGM) coatings on almost all components. To reduce cost and increase efficiency, membrane thickness is the easy aspect to tackle. By combining that with tuning the catalyst composition and loading, Proton OnSite and the project partners are pursuing the best and quickest approach to achieve $2/kg.
- This project (and the U.S. Department of Energy) is solving a huge problem for the hydrogen fuel cell industry: the capital expense around electrolysis systems. Ayers and the team are taking a "holistic" approach and leveraging fuel cell research, mainly decreasing membrane thickness and catalyst loading. This is very ambitious, considering that funding levels are fairly low. This is also supporting others' research. It is not clear why the membrane hydration versus temperature is being studied. It seems that the size and cost of the heat rejection system would also have to be included for fair assessment. Some more clarification would be helpful. The team has done a nice job with the physical characterization and modeling attempt.
- The overall approaches include optimizing the catalyst component, reducing membrane thickness, and improving the structure of the porous transport layer. These approaches address two critical barriers: (1) long-term durability of the electrolysis system and (2) higher defect sensitivity with advanced materials and operation. The approaches to addressing the barriers are effective and closely correlated with each other. The interface characterization that is being done with electrode cross-section imaging reveals the interface between the catalyst layer and the porous transport electrode. The obtained data provides the information needed for MEA system modeling. The simulation model indicates that the relatively thinner membrane can reduce overvoltage of the cell, which supports and is evidenced by the MEA test results. Meanwhile, the thinner membrane's impact on stress and creep is also understudied. The weakness of the catalyst design approach is the reliance on precious group metals, which limits further reduction of the capital cost of the water electrolyzer. It would be better if the team would clearly state the way the current approach could lead to the ultimate deliverable (an advanced electrolysis stack producing hydrogen at 43 kWh/kg and $2/kg H_2).
- The selected approach to evaluate the performance mechanisms for water electrolysis emphasizes a methodical and logical structure. The membrane, coatings, and modeling work done during the second year progressed logically from the catalyst and modeling work done during the first year. It would be preferred to see some discussion of sustained performance. Short-term performance during an innovation activity may not extend into a deployed system. For many electrochemical systems, a 500-hour test barely qualifies as a fabrication check-out test. While such testing may not be in the project scope, it would be beneficial to have some discussion on how the performance gains from this research activity can be transferred to a fielded system.
- Thinner membranes and higher operating temperature are a good opportunity, as long as the durability does not suffer.

Question 2: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- When considering the market maturity of PEM electrolyzers, it seems that, of all electrolyzer types within HydroGEN, PEM might be the only one able to reach $2/kg in such a short period of time. When considering the proposed approach and current results, it seems that this project shall be the only one with proper impact, and therefore it has the largest potential among the projects within HydroGEN.

- This project has the potential to address outstanding cost and performance issues with electrocatalytic hydrogen evolution by evaluating how each component affects overall system performance. For example, results have shown that membranes composed of short-chain polyfluorosulfonic acids with 50–90 micron thickness demonstrated change in hydration at varying temperatures, compared with other compositions. This result implies improved stability and mechanical strength, as well as superior current density from electrolyzer cells constructed with 50- and 90-micron-thick membranes. Additional studies with catalyst dispersion have identified the optimum ionomer dispersants needed, which will prevent catalyst agglomeration and boost overall performance. In addition, both the distribution on the catalyst and electrode porosity need optimization. These studies will identify how to improve overall efficiency and allow for cost-effective hydrogen production through electrolysis.
- This project aligns well with the objective of the DOE hydrogen production target ($2/kg of hydrogen, 43 kWh/kg of hydrogen). As noted in the presentation, the final deliverable is an advanced electrolysis stack producing hydrogen at 43 kWh/kg and at costs of $2/kg. If successful, the project would have a huge impact since the DOE ultimate target would be reached.
- The potential impact is significant, as PEM electrolyzers are well understood and the target decrease in specific energy consumption can have an immediate benefit, which is relatively straightforward to translate to larger systems with higher technology readiness levels.
- The research has high impact on several levels; it is drawing attention to the issues around decreasing the cost of electrolysis systems. The project is also being open and not secretive with the results, which is also very helpful and broadly strengthens the research community and technology.
- This activity both generates new studies and verifies historical characterization studies of the water electrolysis process. The resulting data enables understanding of the process in sufficient detail to adjust the design and fabrication trade space to craft the required performance. It increases the probability that water electrolysis will achieve the production efficiencies and rates from that crafted performance.
- This project aligns well with the targets of the DOE Hydrogen and Fuel Cells Program.

Question 3: Accomplishments and progress

This project was rated **3.6** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project has shown solid data supporting the advancement of the PEM MEA. The impact of membrane thickness on the swelling of the membrane in the hydrated condition is revealed. The 50-µm-thick membrane demonstrates good stability in hydration temperature change. Additionally, the performance of a series MEA with varied thickness is compared. The MEA based on a 50-µm-thick membrane shows the best performance. The optimal ionomer-to-carbon ratio in the system has been found to be 0.05. The novel ink and coating process has been developed, during which the OER catalyst is directly coated on the porous carbon layer by Meyer rod. Characterization of the porous transport layer and cell modeling have revealed the shape of an optimized cell. LBNL is developing a novel fixture that enables the creep study of the membrane and a stress study with the presence of water.
- The project has shown good progress to date. The quarter one (Q1) milestone has been met by understanding the impact of membrane hydration on electrolyzer current density, and short-chain 50-micron-thick membranes have demonstrated current densities over 2 A/cm^2, below 1.9 V, and between temperatures of 50°C and 100°C. The impact of ionomer content on catalyst agglomeration and electrode porosity has been evaluated, and computational modeling shows excellent agreement with the experimentally verified performance. Long-term testing shows relatively stable performance in excess of ~130 hours. The project's future milestones include the following: in Q2, the team will be down-selecting the membrane based on a hydration-state study of mechanical and chemical properties; in Q3, the in operando electrolysis cell will be operational, and two best-of-the-class MEAs will be characterized under two current densities; and in Q4, the go/no-go point of demonstrating 500-hour durability will be achieved. This is the most important milestone because it will allow for the production of hydrogen at $2/kg.
- The improvement in millivolts with the thinner membrane is significant. The project's excellent microstructural analysis is very helpful in correlating the observations. The initial short-term durability data are promising.

- Despite the low funding, the research team has touched on several important parameters affecting electrolyzers and is trying to develop a cohesive understanding. The team has made progress on many fronts.
- This activity is slowly and methodically progressing toward understanding a complex system. Expecting radical advances from this approach undervalues the benefit gained from not missing a key element along the way.
- The project's progress is excellent, but the target is still somewhat far to reach, considering the results presented. However, if proper MEA configuration is found (i.e., thin membrane, catalyst composition, and loading), the project should be able to reach its goals within the time proposed.
- The progress made in fiscal year (FY) 2019 so far has not been as significant as what was achieved in FY 2018. (1) One Q1 milestone was to "understand [the] impact of membrane hydration conditions on electrode performance." While MEA polarization data were presented with membranes hydrated under different temperatures, no deeper analysis was done to check and separate the over-voltages due to membrane conductivity versus electrode performance. In addition, because the MEA tests were conducted at only one temperature (50°C) and not at the targeted 80°C, it may be too early to conclude this study. (2) The delay on the hydration-state study of mechanical and chemical properties (a Q2 task) will postpone the membrane down-selection and further delay Q3 and Q4 tasks. (3) Based on NREL's MEA test results and Proton Onsite's initial data from FY 2018, there is clearly a challenge in maintaining a performance of 1.7 V at 1.8 A/cm^2 for 500 hours. It would be great if the team could come up with potential countermeasures in time to meet the Q4 go/no-go milestone.

Question 4: Collaboration effectiveness

This project was rated **3.4** for its collaboration and coordination with HydroGEN and other research entities.

- The project is effectively leveraging collaboration with other institutions. For example, LBNL is testing hydrated-membrane tensile strength. NREL is developing catalyst ink, evaluating how particle agglomeration scales with ionomer, and helping with catalyst construction. The University of California, Irvine (UC-Irvine) is imaging the catalyst layer distribution in the porous transport layer and comparing it with catalyst on membrane. Combining all these efforts will provide an overarching view of how each component of the cell affects performance. These insights will lead to the optimization of each parameter to maximize cell performance.
- This project well leverages the strengths of the individual partners to characterize the performance and material properties of the elements within this complex system. By utilizing the Energy Materials Network (EMN) nodes as a project backbone, the project may have results that are more effectively disseminated across the EMN network, thereby accelerating research progress.
- The project demonstrates good collaboration along MEA fabrication (Proton OnSite), MEA stress testing (LBNL), novel ink development (NREL), characterization of MEAs (the National Fuel Cell Research Center [NFCRC] at UC-Irvine), and cell modeling (LBNL). It would be great if there were a page that clearly stated the collaboration framework and the shared duties.
- The collaborations within the project team and with HydroGEN appear to be close and productive.
- The team is well selected and working well together, as evidenced by the high productivity.
- The partners' efforts are well integrated into the project.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The proposed future work is generally good and is working toward achieving the planned targets. Parallel efforts shall be made to consider various strategies and prepare back-up options for addressing the durability challenge. This will be critical for the project go/no-go decision, as the testing cycle (500-hour durability) is very long.
- The proposed future work is well organized and clearly shows the duty-sharing of all collaborators. The optimization of the cathode for the electrolyzer is also important. It is suggested that the team also include further optimization of the cathode (e.g., lowering the precious-group-metal loading on the cathode) in

future study, since the cost of the electrolysis stacking system is also an important aspect, in addition to the operational efficiency.

- This is very good future work, although the team might focus more on reducing catalyst costs and doing lifetime testing. It is not clear if there are any plans to study the effects of start–stop cycling that might occur due to intermittent renewables.
- In general, the proposed work will suffice within the concept of this proposal. It would be beneficial to evaluate the X-ray testing outside of the Ohmic region, should the OER become interesting. It would also be beneficial to identify more clearly the selection criteria for the down-selected materials. Efficiency and durability tend to be inversely related, so the balance between the two should be clarified. That clarification may reveal a need for additional endurance or durability testing, pending available resources.
- The project seems to have a good plan moving forward, but at this point the researchers are still trying to understand how the different components work together and affect the overall performance. Future plans include collaborating with the following partners: (1) LBNL, to evaluate membrane hydration, thickness, and temperature; to incorporate microscale features, including catalyst connectivity; and to study the bubble formation effect on current density; (2) NREL, to construct electrodes with low-catalyst-loading inks and provide them to Proton OnSite for testing; (3) NFCRC, to do in situ X-ray radiography at operating conditions of 1–2 A/cm^2; (4) ORNL, to do post-reaction analysis to evaluate catalyst migration within the electrodes and membranes; and (5) Proton OnSite, to tune cell design and conduct operational tests of screened catalysts and components received from NREL for down-selection based on efficiency and durability.
- This is a very effective and relevant use of HydroGEN nodes. The durability metrics should be defined.

Project strengths:

- This project benefits from extensive collaboration that will address multiple aspects of cell performance. The project has shown promising long-term performance, and accelerated stress tests are addressing how the catalysts will degrade at low loading under realistic, dynamic conditions. The team expects to reduce the PGM loading by a factor of 10 compared to commercial electrolyzers, but this may lead to increased catalyst degradation.
- The project's strengths include the leadership of Proton Onsite in the field of PEM electrolyzers, as well as its very well-defined approach. The project team has the combined expertise to perform materials science and reach the proposed goals, and it has vision with regard to specific challenges related to durability testing.
- This project is methodically and systematically characterizing the elements of a complex system. With this process, the risk of missing a key performance parameter is significantly lower. This risk has been further reduced by the team's utilizing acknowledged experts to execute this process across an established collaborative mechanism.
- The project team and involved HydroGEN researchers are very capable and have a wide range of expertise to tackle different types of technical hurdles. Proton OnSite's experience in electrolyzer production is very important in promoting the transfer of research results to commercial products.
- The project demonstrates the promising potential for the newly developed MEA. The project also shows integrated collaboration among all participating teams.
- This project has a good approach, with good use of the national laboratories' capabilities; it is showing promising progress.
- This is a very well-organized team doing focused work. The researchers are making good progress.

Project weaknesses:

- The only weakness of the project is its reliance on high-loading platinum group metals (PGMs).
- The project does not have enough funding to make much progress. It is a strength to leverage fuel cell research, but it might also be a deficit, as it brings in the same groupthink.
- It will be difficult to demonstrate meaningful durability data, considering the time given for the project. The project's weaknesses also include the integration of new membranes with novel concepts of catalyst layers and the conflicts with existing and traditional stack/system designs.

- The durability of the 50-micron membrane was tested to only 140 hours. The durability plot on slide 17 lacks current density information (based on slide 9, a best guess would be 1 A/cm^2), as well as catalyst-loading information; it is unclear whether this represents 10x lower loading. The progress toward the 43 kWh/kg goal has not been explicitly reported.
- This project includes limited discussion on how the data products will transition from the laboratory to field systems with large-scale hydrogen capabilities. Endurance and operational life appear to be low priorities.
- The project team does not seem to be responding to suggestions from previous reviews. The speed of the transfer and translation of the project results to Proton OnSite's MEA preparation process is slow.
- This project may be trying to address too many challenges at once, rather than critically attacking a few specific aspects of cell performance. Continued progress will determine whether the scope should be scaled back to address fewer challenges within one project.

Recommendations for additions/deletions to project scope:

- The team should include operational process fluid pressure as a variable when evaluating the bubble formation of current-density limitation. The team should also include endurance testing beyond 500 hours, where feasible, to characterize the persistence of already identified performance gains. The team should clarify the trade space between efficiency and durability when implementing the catalyst and component down-selection.
- It would be helpful to clearly show the pathway that leads to the ultimate goal of proposed hydrogen production. The team may consider including further optimization of the cathode in an effort to lower the cathode precious-group-metal loading.
- The project focuses on PEM electrolyzers that use precious-metal-based catalysts. As the ultimate goal is to reduce PGMs by 10 times, it would be better to add specific targets for catalyst loadings and to report in the future if progress is made in this direction.
- A chart should be included that shows the progress made toward project goals. The team should also define durability metrics and extend the durability testing of promising MEAs.
- The project is inching around some key issues. It might be useful to do a "lean innovation" or agility study to see what can be done quickly to have high impact and reduce costs, instead of waiting until 2025 for PEM electrolyzers to proliferate.

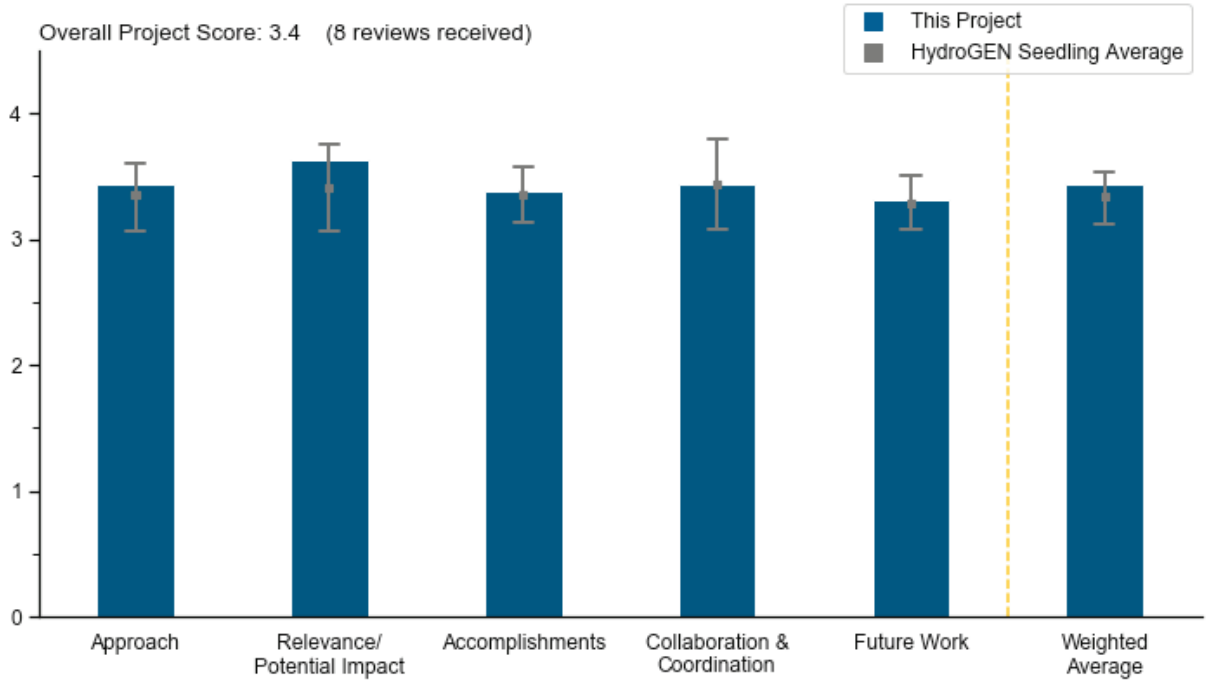
Project #P-156: Developing Novel Platinum-Group-Metal-Free Catalysts for Alkaline Hydrogen and Oxygen Evolution Reactions

Sanjeev Mukerjee, Northeastern University

Brief Summary of Project

The aim of this project is to develop (1) stable, high-conductivity, and high-strength anion exchange membranes (AEMs) and ionomers, (2) stable and active platinum-group-metal-free (PGM-free) catalysts for hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs), and (3) high-performance electrode architectures that together can begin to achieve the low-cost advantages of AEM electrolyzers. This effort is focused on materials development by tailoring synthesis and composites with supporting efforts in computation and characterization. The project work—and collaborations with the University of Delaware (UD), Advent North America, the National Renewable Energy Laboratory (NREL), Lawrence Berkeley National Laboratory (LBNL), and Sandia National Laboratories (SNL)—strives to enable a clear pathway to achieving hydrogen costs of less than $2 per kilogram, with an efficiency of 43 kWh/kg, via AEM-based electrolysis.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- This is a great project that uses much electrochemical, materials, modeling, and synthetic knowledge to provide a path to a Pt-free electrolyzer system. Very logical materials were chosen based on fundamental electrochemical knowledge. Appropriate characterization methods are chosen.
- This project intends to tackle all major technical barriers to efficient hydrogen production from an AEM electrolyzer. While OER and HER catalyst development appears to be the center of the project, the team also targets improved AEM material for electrolysis at higher temperatures, which can further improve electrode performance. This strategy of combining multiple opportunities for improvements can be very effective for achieving higher overall system efficiency.

- The project divides the performance conundrum into logical portions for each group in the team to address, according the strength of the specific group. The issues are clearly identified with appropriate measurement techniques to evaluate progress. By appearances, the work this year focused on the Northeastern University (NEU) Center for Renewable Energy Technology's identifying and characterizing three potential HER catalysts and one OER catalyst, UD's characterizing an alkaline membrane, and LBNL's and SNL's modeling work.
- AEM electrolyzers suffer from a lack of suitable membranes and stable, PGM-free anode catalysts. This project aims to produce stable AEMs, stable PGM-free catalysts for both HER and OER, and optimized electrode architectures. The project's success will help to realize the goal of <$2/kg of hydrogen production. The principal investigator (PI) from NEU will focus on catalyst development to produce PGM-free OER and HER catalysts. HER catalysts will be synthesized by embedding metals into nitrogen-doped carbons. OER catalysts will be synthesized from double-layered metal (oxy)hydroxides, supported on Raney nickel. Performance will be evaluated in half cells and full electrolyzers, and in situ Raman spectroscopy and X-ray studies will be conducted to understand the evolution of the catalysts' oxidation state and structure. The collaborators at UD will design new membranes and ionomers, and Advent North America will focus on electrode fabrication. National laboratory collaborators will facilitate MEA preparation and testing (at NREL), small-angle scattering measurements and modeling (at LBNL), and modeling of interfacial phenomena (at SNL).
- PGM-free catalysts are needed to lower the cost of AEM electrolyzers. This effort is well integrated with the HydroGEN consortium network.
- The approach was highly relevant for overcoming the barrier of AEM electrolysis. The project team has identified key barriers and aims to develop active PGM-free catalysts for electrochemical reactions (HER/OER) and stable electrode structures for AEM electrolysis. Although the objectives appear to have been met, the work is quite ambitious and too broad.
- The presentation mentioned only the AEM barrier on slide 3, while the catalyst is also a critical barrier. The approach includes the development of a new catalyst, novel membrane, and novel electrode, which covers the key features of a projected state-of-the-art AEM electrode.
- The metrics defined to reach the proposed performance make sense only if the use of a support electrolyte is initially defined. If it is, the metrics need to be measured under a specific electrolyte support concentration that boosts overall cell performance.

Question 2: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- As the alkaline electrolysis process currently dominates the market, any innovation that decreases cost, increases performance, or increases life reduces the cost of hydrogen production. This project addressed both the HER and OER reactions that generate ions, as well as anionic conduction rates through the membrane. Success in any of these areas has the potential to reduce hydrogen production costs.
- Low-temperature electrolysis will play a key role in affordable, sustainable hydrogen production in the future. Although AEM electrolysis is at an early stage of research and development (R&D), it is a strong candidate among low-temperature electrolysis technologies. The team's efforts align well with the goals of the DOE Hydrogen Production R&D subprogram.
- This project is closely relevant to HydroGEN's mission to produce hydrogen at low cost and through sustainable processes. As the majority of the cost of electrolytic hydrogen production is from the electricity cost, targeting system efficiency improvements is a good strategy and can have significant impact on the success of the DOE Hydrogen and Fuel Cells Program.
- This project is very relevant to the goals of the HydroGEN consortium. The project aims to develop thermally stable AEMs using earth-abundant and cheap transition-metal catalysts. Success will drastically reduce the costs associated with AEM hydrogen production.
- The goal of the project aligns quite well with the DOE's ultimate hydrogen production target. If successful, the project will be revolutionary since all of the catalysts are PGM-free.

- If successful, this project would provide new low-cost materials for electrolyzers. The work is being done at universities, so it is likely to be published. The materials are well characterized and well understood, so they will provide a baseline for more improvements.
- AEM electrolysis is a promising technology to reach consistent investment cost reduction for electrolytic hydrogen. However, AEMs for electrolyzers have poor performance associated with low durability, which makes it very difficult to reach such an ambitious target. However, the authors are proposing some very interesting AEM concepts, and, if linked well with very active catalysts as demonstrated here, such a target could eventually be achieved within the project. Therefore, if properly pursued, this work could have great impact on the field.
- The durability and validation protocols developed by the Energy Materials Network (EMN) should be universal enough to be useful to all electrolyzer projects and allow for comparisons.

Question 3: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The team has shown good progress toward the overall project goals. For example, the researchers have demonstrated impressive electrolyzer performance for PGM-free catalysts (NiFe/Raney Ni) that exceeds state-of-the-art IrO_2. In situ X-ray absorption spectroscopy (XAS) studies have characterized the evolution of the catalyst's electronic structure as a function of applied potential. Moreover, the team has demonstrated an AEM with almost no change over 1,000 hours at 90°C in 1 M KOH, as measured with nuclear magnetic resonance (NMR). All but one of the remaining milestones have been completed. One milestone was not met because the HER catalysts did not achieve the required target performance, but there is still time for improvements to be made. A catalyst development go/no-go decision point has been met by demonstrating a current density of 500 mA/cm^2 at an overpotential of 150 mV using a PGM-free OER electrocatalyst. Current densities of 800 mA/cm^2 were obtained at an applied voltage of 1.92 V using NiFe/Raney Ni as the OER catalyst and NiCr/C and Ni-cup/C as the HER catalyst. Good thermal stability was observed due to UD's ionomer materials. This met a go/no-go decision point by demonstrating a PGM-free electrolyzer performance of 0.8 A/cm^2 at ≤1.92 V. A molecular model was developed using density functional theory and molecular dynamics simulations to simulate the effects of charging the electrode on the ionomer and mobile species to tie local pH and other resolved quantities to water-splitting efficiency. Small-angle X-ray scattering (SAXS) characterization elucidated the microstructure of the membrane under various hydration conditions.
- The project met its go/no-go milestone target performance for one of the three proposed catalyst systems. The membrane has good temperature stability.
- The project made very impressive progress in the first budget year. Into the second year, membrane material development has already exceeded the planned milestone.
- This project conducted characterization testing of three HER catalysts, compared the performance of an OER catalyst against a traditional PGM catalyst, and started characterization work on an alkaline membrane. A good deal of modeling work was done, some of it not specified within the initial scope of the work. The bulk of the first-year milestones were met, and explanations were provided for the milestones that were only partially successful. Having a clearer discussion on the disparity between the modeling results and experimental results would have been helpful.
- Very good progress has been made on all fronts, despite the large amount of work being done.
- The project has met the AEM and MEA milestone of budget period 1 that was stated last year (0.8 A/cm^2, 1.92 V). There is a significant performance gap between the AEM-based electrolyzer in project PD-156 (0.8 A/cm^2, 1.92 V) and the PEM-based electrolyzer in project PD-155 (1.5 A/cm^2, ~1.76 V [extracted from slide 9]). Because of this, it is recommended that the team clearly outline the pathway from their current status to achieve the milestones noted in the presentation that will lead to the DOE ultimate hydrogen production target ($2/kg H_2, 43 kWh/kg H_2).
- The HER and OER electrocatalyst task has made solid progress laying out a good pathway for the next stage. It would be interesting to see in the next budget year how the combination of those catalysts and new AEMs and ionomers would perform in electrolysis mode. Working with AEM materials with good stability (ex situ) is a significant advantage, as there is no commercial AEM material available now. Catalyst–

ionomer interaction is known to be key in the performance of AEM devices, and thus similar studies including an ionomer stability study with the developed ionomer will be critical in next stage. There is a concern about the use of AEMs with an ion exchange capacity (IEC) of 3.0 mmol/g, which may cause too high of a water uptake (water uptake data is not given in the slides). While AEMs with this high IEC level may enhance ion conductivity and are necessary for meeting the target area-specific resistance, they sacrifice other properties (e.g., mechanical stability, which is equally as important as chemical stability). Typically, these high-IEC AEMs behave like a gel (morphology characterization seen on slide 20) and tend to be partially dissolved in water; this would cause mechanical instability in MEA electrolyzer operation. Although this AEM looks to be chemically stable above 90°C for 1,000 hours in 1 M KOH (by NMR in slide 15), a partial loss of materials due to dissolution cannot be excluded, because IEC measurement by titration and NMR techniques do not count any material loss dissolved into water. On slide 15, NREL's Cl conductivity measurement shows that the PAP-TP-MQN membrane (for which the IEC is 3.0) melted away after the stability test, suggesting that this AEM is (partially) soluble. It is suggested that the team try AEMs with a lower IEC (in the range of 2.5 mmol/g) or adopt a reinforcement strategy for the AEMs to lower water swelling.

Question 4: Collaboration effectiveness

This project was rated **3.4** for its collaboration and coordination with HydroGEN and other research entities.

- This project did an excellent job collaborating between different institutions. For example, catalyst development and membrane development were equally distributed between NEU and UD. SNL constructed models to simulate the effects of charging the electrode on the ionomer and mobile species to tie local pH and other resolved quantities to water-splitting efficiency. LBNL modeled electrolyzer performance in carbonate electrolyte versus in pure water based on experimental data and conducted X-ray scattering and conductivity measurements of the ionomer.
- The project has excellent coordination among different team members, including two national laboratories. The modeling study done by SNL and the SAXS and carbonate-ion-effect modeling study could provide insight into how future materials need to be optimized. Delivering more solid outcomes and results from these collaborations would serve as an important impact of the project.
- This activity distributes work across multiple academic institutions and multiple governmental laboratories. The integrated test results suggest a high data flow rate between the groups.
- This project involves many collaborators from different EMN nodes, and the coordination with the team seems to be going well.
- This is an excellent team with members who have collaborated successfully before.
- This good team has high productivity.
- Modeling by two national laboratories seems to have helped the progress.
- The project demonstrates good collaboration between the development of new catalysts and new AEMs. However, in slide 19, the LBNL modeling shows that the OER overpotential is significantly higher than the HER overpotential, which does not match the experimental result presented (500 mA/cm^2; η [HER] about 300 mV, η [OER] about 150 mV).

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The project's future work will focus on catalyst development, test station and electrolyzer optimization, modeling, X-ray scattering measurements, and durability measurements. These efforts should result in higher-performing catalysts that will ultimately lower operating costs and achieve the desired <$2/kg H_2.
- The proposed future work is clearly delineated and organized between the partners. Within the identified resources, this work focuses on further characterizing the catalysts and membrane, refining computational models, and initiating limited durability testing. It would be beneficial to see an effort that includes developing a plan to transition the lessons learned under this project to the industry.

- It will be interesting to see the origin of the effect or role of the added carbonate feed on electrolyzer performance, which the team is proposing to study. The good mechanical stability and low gas permeability of the AEM under hydrated conditions are also important material properties in water electrolysis, which should be addressed in future study.
- The overall proposed future work is excellent. The critical reasoning for the next stage of the HER catalyst plan (Ni-MOx-Nx) should be clearly stated.
- The project team prepared a good plan for fiscal year 2019 activities. It would be beneficial if demonstrations can be made to show how exactly modeling results help the material or process design.
- There is a good plan for year 2. It is not clear when Advent North America will come into the picture; it may be in year 3.
- The proposed future work is very good overall. It seems less optimistic that the membranes will prove durable. The team should perhaps have a plan in case they fail.
- The team must focus to better establish the benchmark to which the final performance is going to be compared. It is also highly important to perform real durability tests to demonstrate the potential for real applications.

Project strengths:

- The team is composed of expert members from each area, and their approaches are well aligned with the DOE goal of sustainable hydrogen production with a PGM-free electrolyzer.
- This project is strategically attacking challenges associated with both the catalyst and the membrane. The results are extremely encouraging.
- This project is very clearly organized and focused on specific elements: computational modeling and characterizing three HER catalysts, one OER catalyst, and an alkaline membrane. The research team consists of solidly proficient institutions that appear to be collaborating quite effectively.
- This is a very good team that is working together and making progress on developing low-cost materials for electrolyzers. The research is based on fundamental understanding, and the results are published.
- The project's strengths include the team's expertise in electrocatalysis and membrane (AEM) synthesis, as well as novel concepts and strong and solid characterization tools.
- The project team consists of PIs with strong and diversified expertise. The team not only pursues performance improvements but also makes strong efforts to understand the mechanism.
- The team identified a catalyst that meets the go/no-go performance milestone.
- The key strength of the project is the combination of non-PGM with AEMs.

Project weaknesses:

- The project has had difficulty in accessing a solid benchmark and has seen complex chemistry during in situ electrolysis testing. There is a challenge to overcome with membrane stability during in situ operation (>5000 hours), as well as a challenge in electrode and membrane integration (ionomer/binder concept).
- It would have been helpful to include a discussion on the disparity between the computational model and test results.
- It is not clear that the alkaline membrane will be effective. It is simply a very hard problem to develop a new membrane.
- Selecting appropriate AEMs and ionomers would accelerate the progress.
- Better correlation between the simulation modeling and experiment is needed.
- There has not been a report on MEA durability yet.

Recommendations for additions/deletions to project scope:

- The project scope is appropriate.
- It would be beneficial to extend the life testing for longer durations, where resources permit it. Characterizing the integrated cell with a range of concentrations of different electrolytes would be helpful

in identifying any potential design sensitivities that would extend into a system design. It would also be beneficial to develop a plan to transfer the lessons learned into practice.

- The team should include a strategy for the fabrication and scale-up of the new catalyst material.
- It is recommended that the team look at alternative alkaline membranes, possibly Fumatec as a baseline and maybe ionomer membranes (from Holdcroft).
- A more judicious choice of AEM and ionomer materials would accelerate progress in the right direction.

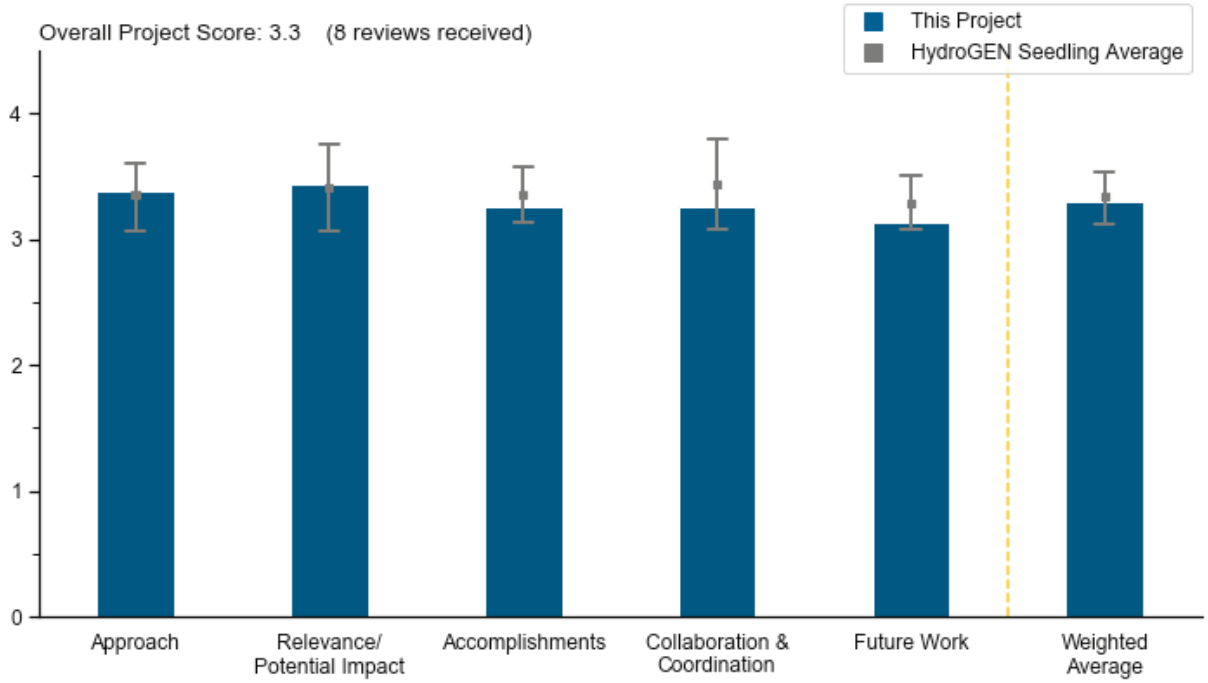
Project #P-157: Platinum-Group-Metal-Free Oxygen Evolution Reaction Catalysts for Polymer Electrolyte Membrane Electrolyzer

Di-Jia Liu, Argonne National Laboratory

Brief Summary of Project

The objective of this project is to lower the capital cost of polymer electrolyte membrane (PEM) electrolyzers by developing low-cost, platinum-group-metal-free (PGM-free) oxygen evolution reaction (OER) electrocatalysts. The project is developing high-activity, high-conductivity, durable metal–organic framework (MOF)-based catalysts via both direct (e.g., solvothermal) and template (e.g., infiltration) synthesis approaches with one, two, or three transition metals. The most promising MOF-based catalysts will then be incorporated in a three-dimensional porous nanonetwork electrode (PNNE) architecture. The goal is to produce durable PGM-free OER catalysts with performance approaching that of current Ir-based PGM catalysts. Argonne National Laboratory (ANL) is partnered with Giner, Inc. (Giner) and University at Buffalo (UB) and is leveraging national laboratories within the HydroGEN consortium.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- This project intends to develop PGM-free OER electrocatalysts to replace Ir-based catalysts in PEM electrolyzers. This is a challenge because there are no commercially available PGM-free PEM anode catalysts that can survive positive potentials. Realizing a PGM-free OER catalyst will dramatically reduce electrolyzer costs. The catalyst of choice is constructed from a Co-containing MOF. This catalyst has shown impressive OER activity in acidic conditions that approaches that of Ir-based catalysts. The electrodes can also be prepared by electrospinning the MOF catalyst to make a porous nanowire-type system. The team is also considering a zeolitic imidazolate framework (ZIF) to create the catalysts. This

approach is unique and appears to show great promise. The catalysts are active and stable in acidic conditions, which has the potential to eliminate the need for PGM anode catalysts.

- This project is rated a 3.5 for identifying barriers and addressing them through project innovation, design, feasibility, and integration with the HydroGEN consortium network. This project attempts to develop PGM-free OER catalysts operating in acid electrolyte. The project uses MOFs containing transition metals (Fe, Co, Ni, Mn, etc.) to screen the best OER catalysts in acid with the lowest overpotential (350 mV at 10 mA/cm^2 in this work). The cooperating partners are from computation modeling, characterization, and industrial water electrolyzer technology backgrounds. More fundamental understanding is needed to reveal why this kind of transition-metal-based OER catalyst can exhibit excellent activity and stability—especially stability—in acid electrolyte. More rationale in screening catalysts is recommended. Understanding the role of each addition is of great significance.
- The goal of this project is to develop PGM-free OER catalysts based on earth-abundant metals and their MOF and ZIF complexes for PEM electrolysis operating under acidic media. As PEM electrolysis is at a stage of near-term commercialization (though currently using Ir for the OER catalyst), a successful outcome of this project would immediately bring significant impact to the mission of the U.S. Department of Energy and HydroGEN.
- PNNE is an elegant approach; it eliminates a major source of catalyst corrosion (carbon). The metrics are clearly stated (slide 8).
- There are three methods adopted here to develop efficient PGM-free OER catalysts in acid. Method 1 and Method 2 appear to be appropriate and deliver decent activity and stability in rotating disk electrodes (RDEs) and good performance in membrane electrode assemblies (MEAs). The development of the ZIF-8-derived catalysts in Method 3 lags behind, showing some activities in RDEs. More importantly, this type of catalyst is carbon-based. This is a big concern since at OER, relevant potential carbon corrosion becomes serious and causes rapid degradation of the catalysts. The Co-based catalysts developed in Method 1 seem to contain graphene during the synthesis, but the principal investigator (PI) mentioned that the vast majority of the graphene was removed at the end. These chosen methods for the synthesis of the catalysts match the expertise of the partners in the team. The characterizations in collaboration with national laboratories and the MEA testing methods are appropriate.
- This work focuses exclusively on the OER reaction based on the interactions of the PGM-free catalysts and polymer membrane. This project appears to be at risk of diluting work across too many collaborative entities. While an intentionally catalyst-focused effort, this work provides little discussion on how the work transitions to other scales of integration or will eventually lead to the targeted savings. At some point, this work should transition to industry and have a path to that end.
- The researchers are studying MOFs, which are materials with which they have a good deal of experience. While the class of materials has activity, there is no real evidence given for why these should be active for the OER. In cells, they have very poor current density (<250 mA/cm^2). It is not clear why the in-band valence structure is important. It is good that the project is using Giner to help with the testing.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The ability to create scalable, PGM-free anode catalysts for PEM electrolyzers could be a transformational development that lowers the costs of water electrolysis. The results presented to date are extremely impressive and encouraging for the realization of PGM-free OER catalysts for PEM operation and production of hydrogen at less than $2/kg.
- The goal of this project is to develop PGM-free OER catalysts based on earth-abundant metals for acidic PEM electrolyzers. As PEM electrolysis is at a stage of near-term commercialization (though currently using Ir for the OER catalyst), the development of low-cost, high-activity, earth-abundant transition-metal catalysts could immediately bring significant impact to the mission of DOE and HydroGEN.
- This project directly addresses the problems of expensive anodic OER catalysts. The state-of-the-art OER catalysts such as IrO_2 and RuO_2 could be replaced if robust OER catalysts worked in both acid and base. The biggest problem of current state-of-the-art catalysts for OER in acid is with their stability. If the

stability issue can be solved, PEM electrolyzers can show their advantages of fast hydrogen evolution reaction kinetics and commercialized PEMs.

- This work is very relevant to reducing the production costs of hydrogen by increasing the efficiency of the OER catalysts and/or replacing the PGM-based catalysts with less expensive alternatives. Reducing the dependence on PGM materials is beneficial only with abundant replacement catalyst materials. The dependence on cobalt leaves this activity exposed to questions about catalyst material availability.
- PGM-free catalysts for low-temperature electrolysis (LTE) are needed to reduce capital cost.
- There is an intrinsic risk involved when targeting the replacement of Ir-based catalysts for PEM electrolysis. Iridium seems to be the only stable element that can be used in this environment. Therefore, the potential for impact in the field is very high, but so is the risk.
- The project demonstrated effective hydrogen production with a PEM water electrolyzer (PEMWE) with a PGM-free anodic catalyst with relatively low overpotentials, which shows good progress aligning with the Hydrogen and Fuel Cells Program and DOE research, development, and demonstration objectives. The lack of fundamental understanding of the activity and information about the catalysts will make further progress difficult.
- It does not look like the MOF catalysts work very well, and there does not seem to be a path for them to perform better. Therefore, it is not clear that there will be much important work from this research.

Question 3: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The team has shown excellent progress by demonstrating the OER performance of PGM-free OER catalysts constructed from Co-MOFs. The team has demonstrated superior stability compared with IrO_2 in accelerated RDE testing in acidic conditions, and co-doping different transition metals into the MOFs has been shown as a way to further improve performance. These multimetallic catalysts show enhanced OER performance above IrO_2 at moderate overpotentials. MEAs constructed from the PGM-free OER catalysts produced a current density of 320 mA/cm^2 at 1.8 V. Ongoing materials characterization using X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM), and density functional theory (DFT) are correlating catalyst structure and composition with performance. Structural studies using a variety of analytical tools are being used to better understand catalytic activity and the aging mechanism for PGM-free OER catalysts in the acidic environment, resulting in mitigation strategies for decreasing degradation rates. The team is well on its way to demonstrating the budget period (BP) 2 overall performance goal of >400 mA/cm^2 at 1.80 V in activity and reducing voltage loss of <100 mV after 100 voltage cycles in durability. The team is also currently investigating ZIFs coupled with carbon nanotubes and polymer scaffolds to further increase OER performance.
- In regard to catalyst activity, last year's ANL-a catalyst had the OER overpotential of 354 mV (as seen in the slide on page 9), which is only 21 mV higher than Ir black (100 mg/cm^2) at 10 mA/cm^2, which has already met the go/no-go milestone. However, this year's best-performing catalyst, LM@ANL-b, has a similar overpotential at 10 mA/cm^2 (as seen in the slide on page 11). Some of them (LM@ANL-b, LL@ANL-b) have a lower overpotential, at 20 mA/cm^2, than Ir black. This is attributed to the second and third additions of transition metals. However, the screening method could be more efficient, and the role of each addition could be clarified. Catalyst durability for ANL-a and ANL-b showed only small voltage losses of 24 mV and 22 mV, respectively, at 10 mA/cm^2 after 10,000 voltage cycles from 1.2 V to 2.0 V (slide 9), which is less than Ir black at 100 µg/cm^2 (88 mV). Regarding the MEA test results, the project team has put its OER catalysts in MEA. The project achieved 320 mA/cm^2 at 1.8 V (in the slide on page 12), exceeding the BP 1 goal of 200 mA/cm^2 at 1.8 V and not far from the BP 1 goal of 350 mA/cm^2 at 1.8 V. It is quite promising, and the team should test MEA durability next.
- The BP 1 goal was achieved. Both ANL-a and ANL-b demonstrated current densities ≥300 mA/cm^2 at 1.8 V. These performances approach the BP 2 goals but have not yet reached them. Reaching the BP 2 goals seems quite likely. There is no clear fundamental understanding of the high OER activity of ANL-a and ANL-b catalysts since it is not clear what the two catalysts are. The PI mentioned the team is currently in the process of either publishing or patenting and will reveal the nature of the catalysts afterwards.

- The project has shown promising progress for both ANL-a and ANL-b. Good durability was demonstrated in RDE testing. The project has met the BP 1 target performance in 25 cm^2 cells.
- The team has made solid progress on the development and characterization of PGM-free catalysts (ANL's Co-MOF and porous nanonetwork electrocatalyst and UB's ZIF-8 catalyst). Some of them have shown very good catalytic activity and durability in RDE and half-cell testing under an acidic environment. However, demonstration of those catalysts in a real PEM electrolyzer MEA is still not sufficient. Building MEAs with new catalysts is not trivial, and a delay in the task of MEA development is understandable. The team has to identify what hurdles they face and suggest strategies to meet them.
- The work focused on characterizing PGM-free MOF and ZIF-8, almost exclusively using RDE testing. The parallel work included alternative manufacturing processes to generate the higher-conductivity catalyst support structures. This activity mostly met two BP 2 milestones and is on track to meet the third. This activity provides the appearance of diffusing the work to the point of obfuscating progress.
- The catalysts perform poorly in the electrochemical cells.

Question 4: Collaboration effectiveness

This project was rated **3.3** for its collaboration and coordination with HydroGEN and other research entities.

- The team has successfully collaborated with Lawrence Berkeley National Laboratory (LBNL) for model simulation and electronic structure calculations. These efforts are modeling the optical properties of the materials in an effort to understand how electronic structure affects electrochemical OER activity. The team has collaborated with Sandia National Laboratories (SNL) for atomic resolution TEM imaging and energy dispersive X-ray spectroscopy (EDX) to quantify local composition and structure. The team has collaborated with the National Renewable Energy Laboratory (NREL) for X-ray photoelectron spectroscopy (XPS) characterization of the catalysts to understand how different catalyst compositions and preparations affect the Co valance state and electronic structure before and after OER testing.
- The team has the following collaborations, which worked out well for the project: (1) computational modeling cooperation at Lawrence Livermore National Laboratory (LLNL) and LBNL, (2) electron microscopy characterizations at SNL, (3) electrode optimization and catalyst characterization at NREL, and (4) industrial partner Giner, which specializes in water electrolyzer technology.
- The team has established good collaboration with other HydroGEN participants, including LBNL (for modeling study to gain insight into the origin of catalyst stability and conductivity), LLNL (for modeling study about charge transfer in OER catalyst), SNL (for scanning transmission electron microscopy [STEM] morphology study of catalysts), and NREL (surface analysis of catalysts). All of these could help the team's effort.
- There is effective collaboration with other national laboratories for modeling and with Giner for in-cell performance evaluation.
- The team is strong and appropriate for what was proposed for implementation. The collaborations with national laboratories are great. The whole collaboration nicely covers all the necessary aspects, including synthesis, characterizations, modeling, and RDE and MEA evaluations. However, there appear to be some disconnections between the catalyst synthesis, performance, and characterizations. The characterizations do not present a clear picture of the catalysts and, together with modeling, do not provide plausible causes accounting for the high OER activity.
- It is good that ANL is working with Giner. The team might also consider working with the fuel cell researchers at ANL (Meyers or Stamenkovic). Research into the prior work on MOFs done by the PI showed surprisingly poor oxygen reduction data in the publication. It was astounding that a group from ANL could be doing oxygen reduction measurements on Pt in sulfuric acid. It is surprising that the work was even published. It does not give much confidence in the alkaline OER data.
- This project has seven collaborating entities focusing on advancing the catalyzed OER. There exists a risk that good work has been spread too widely and is limiting evolving the work to the next scale. At some point, in situ membrane testing needs to replace RDE testing so the project can evaluate the scaling potential of the sub-cell-scale innovations.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The future plans seem appropriate for realizing high-performance, PGM-free OER catalysts for PEM electrolyzers. The stated future plans include synthesizing and evaluating the OER performance of multimetallic MOF catalysts and the potential use of atomic layer deposition for surface doping; evaluating the OER performance of electrospun nanowire-type MOF catalysts; exploring new materials with performance targets in full cell testing; continuing the exploration of ZIF-based catalysts; pushing the performance target higher to 400 mA/cm^2 for the full electrolyzer cell; and continuing to improve fundamental understanding of the structure–function relationship of PGM-free OER catalysts using computation modeling and advanced characterization tools through collaboration with HydroGEN.
- The proposed future work appears to be reasonable and nicely covers all of the work to be conducted, especially the MEA testing and the durability.
- The project has an excellent plan.
- The stated goal of continued focus on catalyst performance in the next fiscal year has merit. However, not identifying a path toward commercialization exposes this project to questions as to how well it aligns with the stated goal of cost reduction. If the goal of this project is to reduce costs, industrial-scale manufacturing processes and integrated cell and stack testing will need to enter into the picture at some point. Those processes may not fit within the project resources, but developing a plan provides answers to difficult questions.
- The planned work seemed to have a lack of focus. The current synthesis methods are already quite efficient and can be used to prepare high-performance catalysts. The key point is to push the MEA performance and to try to scale up the catalyst synthesis. Additional efforts are recommended to understand why those transition-metal-based catalysts can show such high activity and durability in acid.
- In spite of the good progress made in catalyst activity and durability in RDEs, the proposed testing and demonstration in PEM electrolyzer MEAs has been slow. The team should address how to avoid corrosion issues in the catalyst system's carbon matrix under the acidic media of a PEM electrolyzer.
- It may not be worth researching this material any longer.

Project strengths:

- One of the major strengths of this project is in the catalyst development. Both the ANL and UB teams are good at PGM-free catalyst development, and the catalysts developed in this project indeed exhibit promising OER performance in practical PEMWE. This is probably the toughest part of the project since it is not easy to develop PGM-free catalysts for the OER in acid, given that only limited PGM-free materials are stable in acid—and even fewer under such high potentials. In addition, carbon cannot be used to achieve high electrochemical surface area (ECSA) because of the carbon corrosion issue, and not too many alternative supports are stable at such extreme conditions while ensuring high ECSA. It seems like ANL-a and ANL-b, especially the former case, coped with all these issues and delivered decent performance in PEMWE.
- The team has demonstrated a low-cost transition-metal-based OER catalyst. It shows excellent activity and stability in acid. The best, LM@ANL-b, has ~350 mV overpotential at 10 mA/cm^2 (as seen on the slide on page 11). The durability is also supreme. ANL-a and ANL-b showed only small voltage losses of 24 mV and 22 mV, respectively, at 10 mA/cm^2 after 10,000 voltage cycles from 1.2 V to 2.0 V (from the slide on page 9), which is less than Ir black at 100 µg/cm^2 (88 mV). The MEA performance is very encouraging (350 mA/cm^2 at 1.8 V).
- The project has demonstrated excellent activity of PGM-free materials in a non-alkaline environment that is comparable to IrO_2. The future plans seem to be appropriate, and the collaboration is sufficient to understand the underlying structure–property relationships that allow for such impressive OER performance.
- The project's strengths include its ambitiousness, the expertise in MOF synthesis and characterization, and the PEM electrolysis expertise from Giner.
- The project focus is on a narrow, but very important, issue in hydrogen production using PEM electrolyzers. The catalysts developed from this project look very promising, at least in half-cell testing.
- This project focuses exclusively on the replacement of PGM catalysts for the OER.

- This is a strong team; excellent performance has been demonstrated.
- The team has experience with MOF-based catalysts.

Project weaknesses:

- The biggest concern is the lack of information about the catalysts being developed. The presentation did not deliver a clear idea of what the catalysts are, including the element, morphology, active sites, etc. It is understandable that materials may be under publishing or patenting, but this makes it hard to judge the potentials of the developed catalysts. The characterizations are not closely related to the catalyst performance and do not reveal a clear picture of the catalysts. In particular, all of a sudden the STEM shows that the ANL-a has a protective layer of conformal TiO_2 coating that is 1–2 nm thick. This is rather surprising, as this is the first place mentioning that ANL-a contains a TiO_2 layer. In addition, such a thick protecting layer will make active sites inside electro-inactive. This issue needs to be addressed.
- It is difficult to translate RDE results into single-cell testing. There is a short supply of cobalt, the base element of the catalyst proposed here, perhaps even worse than iridium. There may be competition with batteries. Intrinsic low current densities are associated with catalysts for OER other than iridium.
- There is a lack of understanding of transition-metal-based OER catalysts in acid. For example, it is not clear why the stability is better than with Ir black. The screening of the catalysts needs more rationale. The role of the second and third addition metals should be identified.
- The team has very poor electrochemical data in this presentation and a recent history of publishing poor data, despite being at ANL with some of the best fuel cell researchers in the world.
- There appears to be no path toward scaling the innovations or realizing the stated project goal of reducing the cost of hydrogen production.
- More comprehensive demonstration of the developed catalyst at the PEM electrolyzer MEA level is suggested.
- The low current density compared to conventional LTE catalysts means higher electrolyzer capital cost.

Recommendations for additions/deletions to project scope:

- This project would benefit from a plan that addresses how the innovations will meet the stated project goals of reducing the cost of producing hydrogen. At a minimum, this plan should include how to implement the innovations beyond a sub-cell level and how to deliver the stated goal of reducing the cost of hydrogen production on a larger scale. Evolving the catalyst testing beyond the RDE level and implementing more endurance and cell-level testing of the developed catalysts will identify viable catalysts for further scale-up. The characteristics and properties of those catalysts can be fed back into the modeling and catalyst development efforts to further this iterative process.
- It is recommended that the team add the necessary information of the catalysts developed and make sure that carbon is not the essential part of the catalysts; ideally, there should not be any carbon in the catalysts to be assembled in the MEA. The team might try other transition metals such as Mn, Fe, and/or Ni for catalyst development.
- The team should change the target of 1,000 A/cm^2 at 2 V to 1,000 A/cm^2 at 1.6–1.7 V. This can be accomplished by playing with membrane thickness. MOFs will have stability issues at such a high voltage.
- An investigation of mechanisms of transition-metal-based OER catalysts in acid is recommended. This can lead to more efficient catalyst screening.
- More effort on characterization and a demonstration of the developed catalyst at the PEM electrolyzer MEA level is suggested.
- The performance of the ANL cells is well below that published by the Asahi Kasei Corporation. (Yasuhiro Nakajima, Norikazu Fujimoto, Shinji Hasegawa, and Taketoshi Usui. "Advanced Alkaline Water Electrolyzer for Renewable Hydrogen Production." *ECS Transactions* 80, no. 10 [2017]: 835–41.) At 1.75 V cell potential, Asashi Kasei reports current densities on the order of 600 mA/cm^2 at the system level, while this team reports 200 mA/cm^2. There is no clear path to meeting the state of the art for alkaline, never mind for acid electrolysis.

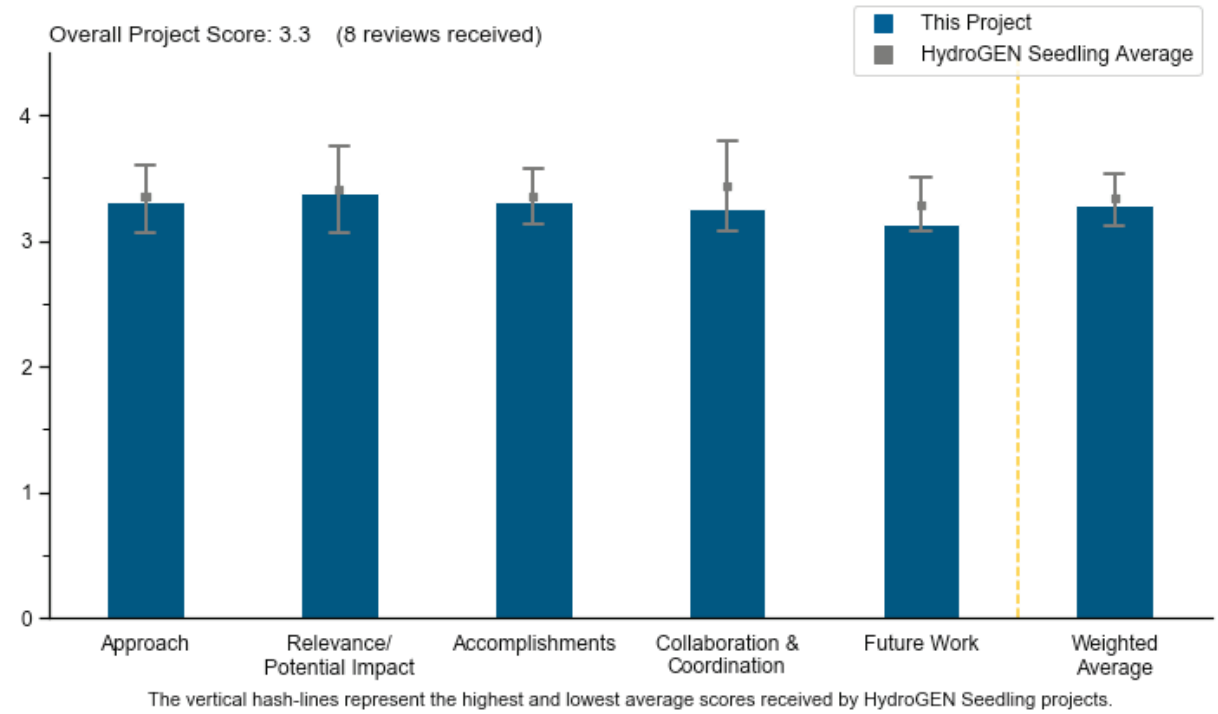
Project #P-158: High-Performance Ultralow-Cost Non-Precious-Metal Catalyst System for Anion Exchange Membrane Electrolyzer

Hoon Chung, Los Alamos National Laboratory

Brief Summary of Project

The primary objective of this project is to develop low-cost, active, and durable platinum-group-metal-free (PGM-free) oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) catalysts with high performance in an anion exchange membrane (AEM) water electrolyzer. The HER and OER catalysts being developed are based on Ni-La alloys and $LaSrCoO_3$ (LSC)-based perovskite materials, respectively. The catalysts and electrodes will be carbon-free, and a pure water feedstock (i.e., no added electrolyte) is targeted. In addition to utilizing HydroGEN Consortium national laboratory capabilities, the project team will partner with Pajarito Powder, LLC (Pajarito) for catalyst scale-up activities.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.3** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- A key challenge with AEM electrolyzers is how to eliminate salt or alkaline solutions and split pure water. This project aims to develop PGM-free OER and HER catalysts that demonstrate high activity in the absence of alkaline solution. This will eliminate the cost and complexity of electrolyzer systems with an anticipated goal of <$2/kg of hydrogen. The main goals of this project are to reduce the overpotential and costs associated with traditional HER and OER catalysts. The team's plan centers on designing high-activity, PGM-free OER and HER catalysts for water splitting in the absence of alkaline electrolyte. This project will use AEM cell design for water electrolysis in the absence of alkaline electrolyte. Using water instead of alkaline electrolyte will allow the use of stainless steel current collector to stainless steel, which is estimated to eliminate 75% of the cost compared to polymer electrolyte membrane (PEM) technology. Finally, the team hopes to replace the Nafion membrane with a hydrocarbon membrane. The approach

involves synthesizing PMG-free HER and OER catalysts to promote water splitting. The HER catalyst is based on a NiLa system, and the OER catalyst is based on a perovskite catalyst. The perovskite OER catalyst shows impressive performance compared to IrO_2. Electrolyzers using the perovskite OER catalyst can reach a maximum current density of ~240 mA/cm^2 in water at 80°C, with stable performance at over 100 hours. This performance can be boosted to over 450 mA/cm^2 with 0.1 M NaOH electrolyte.

- The project aims to enable low-cost hydrogen production via the development of non-PGM-based OER and HER catalysts for use in AEM electrolyzers. The catalyst materials, LSC-derived perovskites for OER and LaNi alloy for HER, are not new to the research community. The investigation of catalyst–ionomer interaction and the behavior of the catalysts in AEM electrolyzers can provide valuable knowledge for improving the design of catalysts and membrane electrode assemblies (MEAs), with higher efficiency and lower capital cost.
- This project attempts to develop LSC-based materials for operation in alkaline-free water electrolysis systems. The project team added an organic cation (butyltrimethylammonium [$BTMA^+$]) in the electrolyte to promote the OER in perovskite-based catalysts. It is worthwhile to explore those substitutes for alkaline electrolyte. The ionomer–catalyst interface is worthy of exploring.
- The project is taking a very ambitious but decisive approach to use deionized (DI) water for electrolysis operation. This intrinsically limits performance but has a decisive impact on durability. If the project team manages to solve the issues related to AEM conductivity, it would lead to a very important impact on the field.
- The team proposes to develop PGM-free, Ni-La alloys for HER catalysts and LSC-based perovskite materials for OER catalysts for AEM electrolysis. Los Alamos National Laboratory (LANL) will develop the catalysts, and the project's industrial partner will work toward the scale-up production of catalysts. Phase I was focused on catalyst development, while Phase II is more focused on catalyst–ionomer interaction.
- This project has improved its approach since last year. There now exists a clear and logical path for development, supported by solid rationale and cost justification for the work on PGM-free catalysts, water-based process fluid, and alkaline membranes.
- The team is studying a low-performing, non-precious-metal catalyst. Their method is to benchmark against iridium catalysts, but there seems to be something wrong with their iridium baseline, as the cells on slide 8 perform very poorly. As a reference, the authors might look at figure 3 in the following paper by Asahi Kasei Chemicals, Co. (AKC): *ECS Transactions*, 80(10), 835–841 (2017). (There might be some better references out there, but this seems reasonable.) AKC shows performance at the system level, with 600 mA/cm^2 at 1.7 V/cell. Chung reports a cell with iridium at 250 mA/cm^2, in a small cell. It seems that LANL should benchmark project results against a reasonable standard. (This was an old problem in fuel cell catalysts that has been fixed.) The following paper might also be useful for methods (although stationary drying cannot be used for the preparation of electrodes; rather, rotational drying is used): https://doi.org/10.1002/adma.201806296
- The project makes good use of HydroGEN nodes.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- This project is extremely relevant to HydroGEN's goals of inexpensive hydrogen production. One main problem with PGM-free OER catalysts is low activity or dissolution in neutral or acidic conditions. This project demonstrates a perovskite oxide-based OER catalyst that demonstrates excellent water-splitting activity and stability in alkaline-free conditions. The continued improvement of performance is on track to meet the goal of <$2/kg of hydrogen.
- If every milestone is met, this project can simplify the overall system and minimize carbon in the MEA to improve longevity. The bipolar assembly and MEA represent the highest costs of a PEM stack (35% and 18%, respectively). If met, the milestones can reduce 75% of this cost and enable lower-cost catalysts. This project did not use PGM-based catalysts, which may help reduce the cost of catalysts. Ionomer–catalyst interfacial studies can reveal an ionomer-poisoning effect on catalysts; approaches can be devised to address this issue.

- Enabling a water-recirculating alkaline electrolyzer to generate hydrogen nearly as efficiently as a PEM electrolyzer significantly simplifies the wetted-materials issue for electrolysis systems. If the reaction pH is significantly increased, less expensive materials may be used in the process stream. Recirculating pure or nearly pure water can impose known and well-understood challenges that have well-established mitigation options. Replacing PGM catalysts with a more readily available catalyst material reduces cost and eliminates risks of a supply shortage.
- Compared to a PEM electrolyzer, an AEM electrolyzer can offer significant cost reduction by allowing lower-cost bipolar plates and electrocatalysts. AEM electrolysis offers a number of advantages over alkaline electrolysis based on a strong KOH solution. Overall, AEM electrolysis is less mature than those two hydrogen production technologies; however, it could offer significant impact if successfully developed and adopted commercially.
- The project aligns well with HydroGEN's mission to develop an electrolytic process for low-cost hydrogen production. The use of non-PGM catalyst materials and the improvement of their performance can lead to higher system efficiency and lower stack cost. The potential to use only water feed also simplifies the system design.
- The project is high-risk and has a challenge in reaching significant cell performance, but there will be an extreme impact if the team can obtain performance by tuning electrode and AEM structure.
- There is promise of lower capital cost in the long term, but there is a lower technology readiness level than with PEM and alkaline technology.
- It is unclear why the project attempts to use useful materials and develop electrochemical methods when the approaches are really outdated compared to work being done in the fuel cell community. It is not certain that the methods and results are very good or will have much staying power.

Question 3: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- From last year, the team has demonstrated significantly increased electrolyzer performance with a five-fold increase in current density compared with fiscal year (FY) 2018 results. The project has demonstrated impressive OER performance with a PGM-free, perovskite-oxide-based catalyst in both three-electrode and electrolyzer configurations. The team has also evaluated the performance of several ionomer binders to optimize electrocatalytic OER performance. Water electrolysis in the AEM cell reached 243 mA/cm^2 at 1.8 V and 80°C and showed good stability over 100 hours at 100 mA/cm^2. Continued progress is required to meet future milestones, including synthesizing a new NiLa(Zn) HER catalyst that produces 50 mA/cm^2 at 200 mV overpotential for use in an electrolyzer device. The FY 2019 go/no-go performance of 100 mA/cm^2 at 1.8 V has been exceeded, with a maximum performance of 243 mA/cm^2 reached at 80°C. The team is on track to meet the goal of obtaining a PGM-free HER catalyst with degradation similar to Pt.
- The current density with AEM achieved 119 mA/cm^2, 175 mA/cm^2, and 243 mA/cm^2 at 60°C, 70°C, and 80°C, respectively, exceeding 100 mA/cm^2 at 1.8 V. It is worth noting that the project team exceeded last year's record of 119 mA/cm^2. By changing the electrolyte environment from water to 0.1 M NaOH, current density can be brought to 452 mA/cm^2. At 100 mA/cm^2, 1.8 V for 100 hours, the catalysts show almost no degradation in AEM. The team also developed a gas diffusion electrode (GDE) electrochemical cell approach, which successfully identified the AEM ionomer effect on OER performance, demonstrating the merits of using perovskite plus a benzyl trimethyl ammonium hydroxide (BTMAOH) electrolyte.
- Compared to Phase I when the team focused on the evaluation of catalyst performance by rotating disk electrode (RDE), the team has made significant progress in Phase II and has shown good performance and durability of the catalysts in AEM electrolysis (with pure water and no added salt). Furthermore, by developing a novel GDE electrochemical cell experiment, the team has identified the effect of AEM ionomer on OER performance and studied a diverse range of catalyst–ionomer interactions.
- This project demonstrated improvements in both OER and HER activity using non-PGM catalysts. Two budget period 2 milestones were met, with expected progress made toward the two remaining milestones. Testing was completed at the RDE stage and evolved into single-cell testing for further characterization. Significant progress was made in identifying the influence of the catalyst–ionomer support on catalyst activity.

- The project is on track to meet the planed performance milestones for Phase II. It was very impressive that the project achieved additional improvement on OER catalyst performance and showed stability over 100 hours. It would be very beneficial for the project team to conduct deeper material characterization and analysis to understand the mechanism behind these improvements.
- The project team has made good improvement with the water-feed system.
- The project team has improved catalyst performance and studied interactions with ionomers, but the electrochemical performance is very poor.

Question 4: Collaboration effectiveness

This project was rated **3.3** for its collaboration and coordination with HydroGEN and other research entities.

- This project has demonstrated good collaboration with the other institutions. Sandia National Laboratories is working on AEMs and ionomer synthesis and has planned in situ X-ray photoelectron spectroscopy (XPS) to characterize catalyst–ionomer interactions. National Renewable Energy Laboratory (NREL) is working on AEM water electrolysis testing and materials characterization, using XPS/ultraviolet photoelectron spectroscopy (UPS) to analyze fresh and tested AEM electrolyzer electrodes. Lawrence Berkeley National Laboratory is planning for in situ X-ray characterization.
- This project evidently made effective use of the HydroGEN nodes based on the progress since last year. The group includes two major partners, collaborating with three national laboratories on four network nodes. The analytical and modeling tools, along with the characterization testing from the network, influenced catalyst and membrane design.
- The project team has excellent cooperation with five nodes, consisting of catalyst development, catalysts and organic interfacial study, and MEA fabrications. Two teams have been added on characterizations.
- The project team consists of a good combination of experts from different areas. The project also effectively leverages multiple nodes available at HydroGEN. As this is a fundamental research project, working with multiple nodes can bring synergistic effect for all participants.
- This is a good use of HydroGEN nodes, especially the NREL in situ testing.
- The collaboration between the project team and the HydroGEN nodes seems to be strong and effective.
- The project team needs to increase relations toward electrode fabrication and single-cell testing partners.
- There is no clear evidence in the presentation of collaboration with Pajarito.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The proposed future work is centered on (1) understanding the phenomena that occur at the catalyst–ionomer interface using in situ and ex situ XPS and x-ray absorption spectroscopy (XAS); (2) conducting GDE electrochemical cell studies to evaluate how catalyst–ionomer interactions impact catalytic activity; (3) modifying catalyst composition based on catalyst–ionomer interaction studies to further improve performance and stability; and (4) optimizing catalyst–ionomer ratios to maximize electrolyzer performance.
- The team proposes to better understand the ionomer–catalyst interface by using in situ and ex situ ambient pressure XPS (AP-XPS), XAS, and GDE electrochemical cell technique. It is essential to understand the degradation mechanism brought on by the ionomer. The team also proposes to develop a new category of catalysts and optimize the combination of catalysts and ionomer. This is a good direction to push the performance.
- The project team has a clear plan to achieve the planned milestones for Phase II. Deeper analysis and understanding of catalyst–ionomer interaction will provide valuable insight for future catalyst layer design. Perovskites are fundamentally non-conductive materials. The project team shall consider strategies to address potential ohmic loss at higher current density (i.e., 1 A/cm^2) in the absence of carbon.
- With identification of catalyst–ionomer interaction as a potential reason for poor durability of AEM electrolysis in Phase II, in the next step, it would be logical to think about mitigating strategies by modifying catalysts and/or ionomers.

- The project team needs to better define the tasks to reach better cell performance when using DI water. It is not clear what the specific tasks are for tackling difficulties in ionomer integration during electrode manufacturing.
- The Pajarito effort is very important. Presenters are asked to include who will do what on future Proposed Future Work slides.
- The proposed future work is more of the same research. It is unclear why the project team is studying catalyst–ionomer interaction for a poor catalyst.
- The future work focuses on catalyst–ionomer interface issues without suitably addressing the membrane or ionomer–membrane interface issues.

Project strengths:

- The team developed a series of PGM-free, perovskite-based OER catalysts that show promising performance (with 119 mA/cm^2, 175 mA/cm^2, and 243 mA/cm^2 at 60°C, 70°C, and 80°C in AEM, respectively, and almost no degradation at 100 mA/cm^2, 1.8 V for 100 hours). The team also demonstrated the significance of electrolyte in base and tried to understand the interfacial interaction.
- The project has a strong collaborative network focusing on the integrated cell-level work for an alkaline-based electrolysis system. Utilizing pure water, rather than a chemical solution, degrades performance but also has the potential to reduce the operating and capital costs of a production system.
- The project addresses important barriers for achieving low-cost hydrogen production with an AEM electrolyzer, especially with an emphasis on catalyst–ionomer interaction. Based on current progress, it seems there is a high chance that the team can achieve the planned milestones.
- This project has successfully identified PGM-free OER catalysts that demonstrate high current densities in the absence of alkaline electrolyte. Continued progress should provide fundamental understanding of the catalyst–ionomer interface and lead to even higher system performance.
- This is a new concept for Pt-free catalysts. There is interest in looking at the interaction between the catalyst and the ionomer.
- The project is well organized and has demonstrated solid progress with good scientific understanding.
- The project team has demonstrated progress with a challenging materials/operating system.
- The project team's strengths include its experience in PGM-free catalysts.

Project weaknesses:

- More attention should be paid to the alkaline membrane that enables the anionic communication between the OER and HER catalysts. It does not benefit this activity if the highest-performing catalyst–ionomer combination is incompatible with the anionically conductive membrane.
- The project's weaknesses include a lack of expertise in electrolyzer testing (single-cell), electrode manufacturing, and the not very clear path toward solving the triple-phase boundary in the electrode (with DI water operation).
- The project team has three weaknesses: (1) they have poorly performing catalysts, (2) they benchmark their performance to poor results for standards, and (3) their electrochemical methods are poorly validated.
- Evaluating the cost of the proposed MEA is necessary. The cost of the perovskite and electrolyte also needs to be taken into consideration.
- The project has a low-current-density target of 100 mA/cm^2 that translates to a high electrolyzer capital cost.
- While substantial progress has been made, the performance of the OER catalyst developed in this project is still lower than catalyst materials reported from other projects and previous literatures.
- The contribution from the industry partner is less clear until Phase II.

Recommendations for additions/deletions to project scope:

- The project uses mainly electrochemical testing methods. It could be beneficial for the team to consider more diversified tools—for example, more surface-sensitive and in situ material characterization approaches—to gain additional insights.
- The authors should get some advice from fuel cell researchers on how to do better electrochemical measurements. The team should also focus on developing a reasonable benchmark for the standard materials used in alkaline electrolyzers.
- The project team should continue utilizing the Energy Materials Network to leverage existing work and focus efforts on unaddressed issues. For this project, this holds true for the gas diffusion layer interface questions and the AEM properties.
- It is recommended that the team define clear mitigation strategies of the problems that were identified in Phase II in order to move forward.
- The increasing current density should be the major emphasis.
- It is recommended that the project have a cost analysis of materials and MEAs.

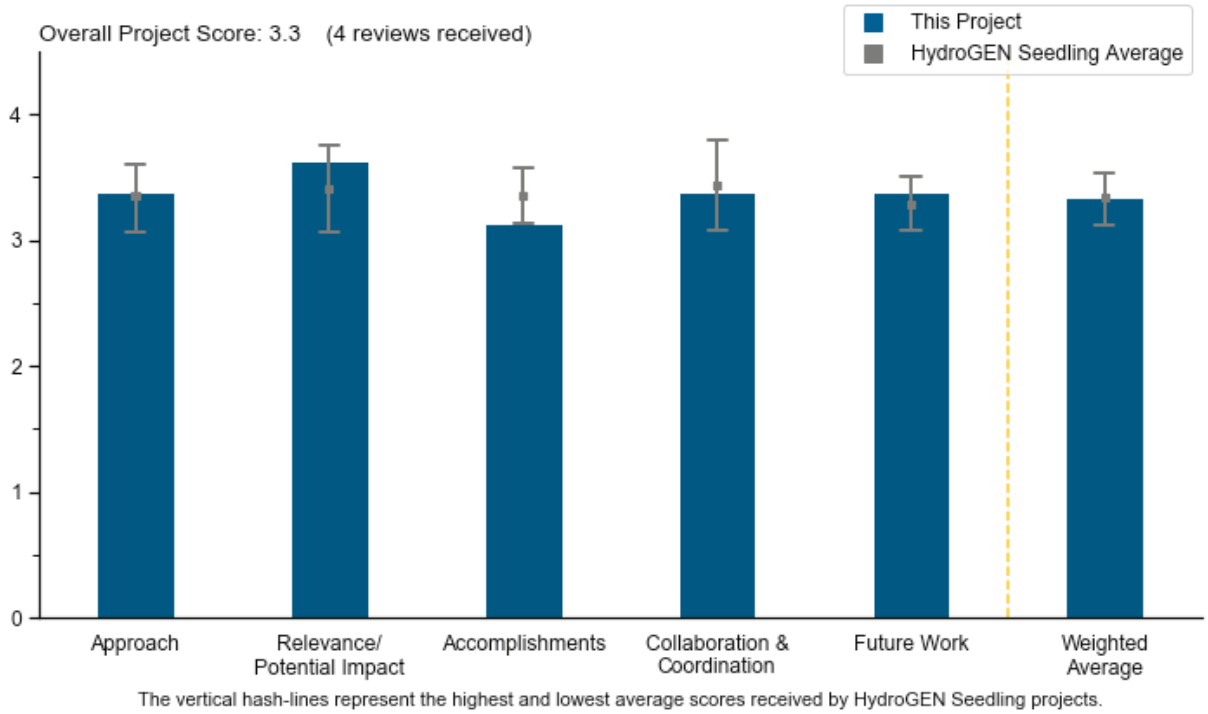
Project #P-159: Scalable Elastomeric Membranes for Alkaline Water Electrolysis

Yu Seung Kim, Los Alamos National Laboratory

Brief Summary of Project

The objective of this project is to develop stable, high-performance, and economically affordable alkaline anion exchange membranes (AEMs) for water electrolysis operation. A low-cost synthetic method based on acid-catalyzed condensation reaction (Friedel–Crafts alkylation) will be developed to fabricate the styrene-based triblock copolymers based on polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene (SEBS) to replace the prohibitively expensive metal-catalyzed reaction route. The project team, which also includes Rensselaer Polytechnic Institute (RPI) and Proton OnSite, aims to develop economically viable elastomeric ionomers having conductivity at least equivalent to polyaromatic electrolytes, with much-improved mechanical properties.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.4** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The project focused on developing low-cost hydroxide exchange membranes for alkaline water electrolysis. The team addressed three key barriers: membrane durability, hydroxide conductivity, and mechanical property. Through rationally designed modification of chemical structure and fabrication method, the team successfully demonstrated the membrane (SES25-TMA-1.7) that met the durability (0% loss of conductivity after 300 hours in 1 M NaOH at 80°C), conductivity (42 mS/cm at 30°C), and mechanical property (2091 MPa × %) milestone. In addition, through the collaboration with HydroGEN, the team observed the formation of acidicphenol, which could be the durability-limiting factor for alkaline electrolyzer. This finding would guide further improvement of the overall device durability through ionomer modification. However, more membrane characterization data—for example, the gas permeability of the membrane—at budget period 1 (BP1) would be helpful. Additionally, the developed AEM

electrolyzer model showed that the overpotential from oxygen evolution reaction (OER) was much larger than that from hydrogen evolution reaction (HER), which deviated from experimental result.

- Alkaline electrolysis suffers from a lack of suitable, commercially available AEM membranes. This effort is exclusively focused on developing stable and scalable AEM membranes for eventual commercial production. The approach is to use evaluate different membrane chemical structures than what is used with state-of-the-art fuel cell membranes. The hope is to prevent degradation of typical AEM membranes by preventing phenyl degradation. The innovation here is developing a method for scalable synthesis and membrane-casting to make it more cost-effective. The specific technical barriers and challenges this project will overcome are membrane stability in alkaline electrolyte, hydroxide conductivity, mechanical properties, and AEM performance and durability. The membrane chemical structure is not new, but the team is developing methodologies for preparing the membrane in a scalable method so that it can be cost-effective. The project's approach centers on producing membranes using styrene–ethylene–styreneblock copolymers that are synthesized by an inexpensive acid-catalyzed route. The added benefit is expected to be a reduction in cost through the elimination of the expensive metal catalysts used in state-of-the-art membrane synthesis routes.
- This project has a clear objective to advance the alkaline membrane material technology, with all work focused toward generating and characterizing that material. In particular, this work evaluates the fabrication processes of membrane materials, then characterizes the hydroxide conductivity, water content, and material toughness. To complicate the project results, this project utilizes a non-traditional definition of toughness (stress times strain), rather than the traditional definition (area under the stress–strain curve).
- The selected block co-polymer synthesis route has multiple benefits.

Question 2: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- This topic is relevant to HydroGEN and extremely important for the alkaline hydrogen evolution field. Commercially available AEM membranes are limited to a few suppliers, and membrane supply and stability are issues. This project will further commercialization of AEM membranes, which are limited in the open market. Moreover, success will bring AEM electrolysis to the same technology readiness level as polymer electrolyte membranes (PEMs). AEM electrolyzer anode catalysts do not need iridium and can be orders of magnitude less expensive than PEM catalysts. Moreover, the flow field can be made from stainless steel, rather than more expensive titanium. These benefits will lower the system cost and allow production of hydrogen at or below $2/kg.
- Alkaline water electrolysis typically uses platinum-group-metal-free catalysts and low-cost stack components, and therefore the capital cost of hydrogen production is significantly reduced. However, the critical drawbacks of alkaline electrolysis are the conductivity and durability of the hydroxide exchange membrane (HEM). This project directly addresses these critical drawbacks by demonstrating a low-cost synthetic route to high-performance and durable HEMs. The improvement of stability and hydroxide conductivity of HEMs enables the pathway to low-cost hydrogen production in alkaline conditions.
- The higher pH of the alkaline electrolysis chemistry, compared to the acidic chemistry, enables a wider range of wetted materials. This significantly reduces the cost of the components within an electrolysis system. The alkaline membranes traditionally lack the durability or performance required for commercial high-pressure electrolysis systems. Generating a high-pH polymer membrane with sufficient durability and performance to compete with the acidic polymer membranes at the cell level would merge the mechanical lessons from the high-pressure PEM systems with the low-cost materials from the alkaline systems.
- The promise of reducing electrolyzer capital cost is appealing, assuming that the current density of PEM electrolyzers can be matched.

Question 3: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The team has shown good progress. All fiscal year (FY) 2018 milestones have been met, and now the team is looking at the chemical structure to try to improve conductivity and water-uptake properties. The project has met membrane conductivity requirements, and strain testing has shown good structural stability. The team is trying to further improve mechanical properties through crosslinking within the chemical structure. The secondary electron spectrum (SES) copolymer showed no chemical degradation over 300 hours in 1 M NaOH, with good conductivity and mechanical toughness. An AEM electrolyzer model has been developed to predict system performance and improve understanding of how pH at the catalyst–ionomer interface can impact HER and OER performance.
- The project team successfully demonstrated the membrane (SES25-TMA-1.7) that met the durability (0% loss of conductivity after 300h in 1M NaOH at 80°C), conductivity (42 mS/cm at 30°C), and mechanical property (2091 MPa × %) milestones. The team also demonstrated a crosslinking strategy to improve the mechanical property further. The XL100-SES25-TMA-1.7 membrane has conductivity comparable with SES25-TMA-1.7 but exhibits a high tensile toughness of 6055 MPa × %. The project also identified a limiting factor that affected the durability in alkaline water electrolysis. These results help guide the future improvement on HEMs, as well as the ionomer.
- The project down-selected to a preferred membrane, synthesized and characterized an ionomeric binder, and demonstrated polyolefinic SES co-polymer with chemical stability and high ion conductivity. From the presentation materials, it remains unclear what milestones pertain to BP1 and BP2. This complicates the ability to evaluate progress.
- The project has shown successful polymer synthesis with promising properties.

Question 4: Collaboration effectiveness

This project was rated **3.4** for its collaboration and coordination with HydroGEN and other research entities.

- The major project partner, Los Alamos National Laboratory (LANL), worked on the identification of performance and durability limiting factors for AEM electrolyzers while RPI focused on polymer membrane fabrication and characterization. The team planned to collaborate with an industrial partner (Proton Onsite) to demonstrate electrolyzer performance. The team worked closely with the Lawrence Berkeley National Laboratory (LBNL) to carry out comprehensive studies on the SES membrane, as well as AEM performance modeling. To validate the improvement of the membrane in alkaline water electrolysis, NERL would be involved to perform the AEM performance evaluation. The overall collaboration is efficient.
- The project has good collaboration across the HydroGEN nodes. For example, LBNL is working on X-ray scattering characterization, microelectrode studies, and AEM performance modeling; Sandia National Laboratories (SNL) provided a baseline AEM for comparison; and the National Renewable Energy Laboratory (NREL) is evaluating AEM performance.
- There is good collaboration with RPI and Energy Materials Network (EMN) nodes. LBNL, SNL, and NREL collaboration will be very important for performance and durability validation.
- The presentation materials suggest that collaborative activity occurs just within the national laboratories. There is solid evidence of strong utilization of the EMN nodes, including LBNL, NREL, and SNL, to fabricate and characterize materials.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The project's future plans seem reasonable for achieving a target AEM performance of 1 A/cm^2 at 2 V with less than 0.2 mV/h degradation during a 300-hour electrolysis test. The future plans involve optimizing ion exchange capacity, block size, cationic group, and crosslinking density of SES membranes to improve

performance. The project's future plans include completing AEM electrolyzer degradation studies compared with optimized membranes produced in this study. In FY 2020, the team will down-select the most promising materials based on performance, optimize the electrolyzer operating conditions, and begin scaling the synthesis of membranes and ionomers.

- The future work consists of further developing the anionic polymer and conducting performance and durability testing on ionomers and AEM electrolysis membranes. As the target does not specify the process fluid (pure water versus solution), the target membrane electrode assembly performance may or may not be relevant. It would also be helpful to have a list of BP2 milestones to compare predicted progress to actual progress.
- The team planned to focus on the crosslinking SES and full device testing for the year 2019. Down-selection of AEM and ionomer, as well as scale-up fabrication, would be carried out in 2020. The planned work would help advance the proposed technology.
- Data at 1 Am/cm^2 and >1,000-hour durability test is highly anticipated.

Project strengths:

- This project heavily utilizes the strengths of the EMN to rapidly develop a viable anionic polymer for use as a solid polymer electrolyte in an alkaline electrolysis system.
- This project has shown good progress toward developing a scalable and stable AEM membrane. Good collaboration with other national laboratories has allowed for characterization of membrane structure and performance.
- The major strength of the project is that it has demonstrated a low-cost synthesis approach for durable and conductive HEMs.
- The project's strengths include its interesting approach to polymer synthesis.

Project weaknesses:

- The presentation material does not clearly define the use of a nontraditional definition of mechanical toughness. Traditionally, toughness is the area under the stress–strain curve. Applying a direct multiplication of the stress and strain inaccurately inflates the results. Currently, the alkaline membrane durability is a major limiting factor to the implementation of a high-pressure alkaline electrolysis system. It would be beneficial to standardize the nomenclature and testing processes so that materials can be consistently characterized. This permits an accurate assessment of the suitability of a material for a particular application.
- The project's weaknesses include the lack of cost evaluation of the proposed technology and yield comparison to prove the benefit of the proposed synthesis method.

Recommendations for additions/deletions to project scope:

- It is recommended that the project team do a cost estimation on synthesis and compare it with the state-of-the-art approach. A gas permeability test of the membrane is recommended for membrane characterization. More details should be provided on how modifications of the ionomer can help solve the effect of pH on durability.
- The project team should continue the effective use of the EMN nodes and standardize measurement processes and nomenclatures to enable consistent comparison of results across the network.

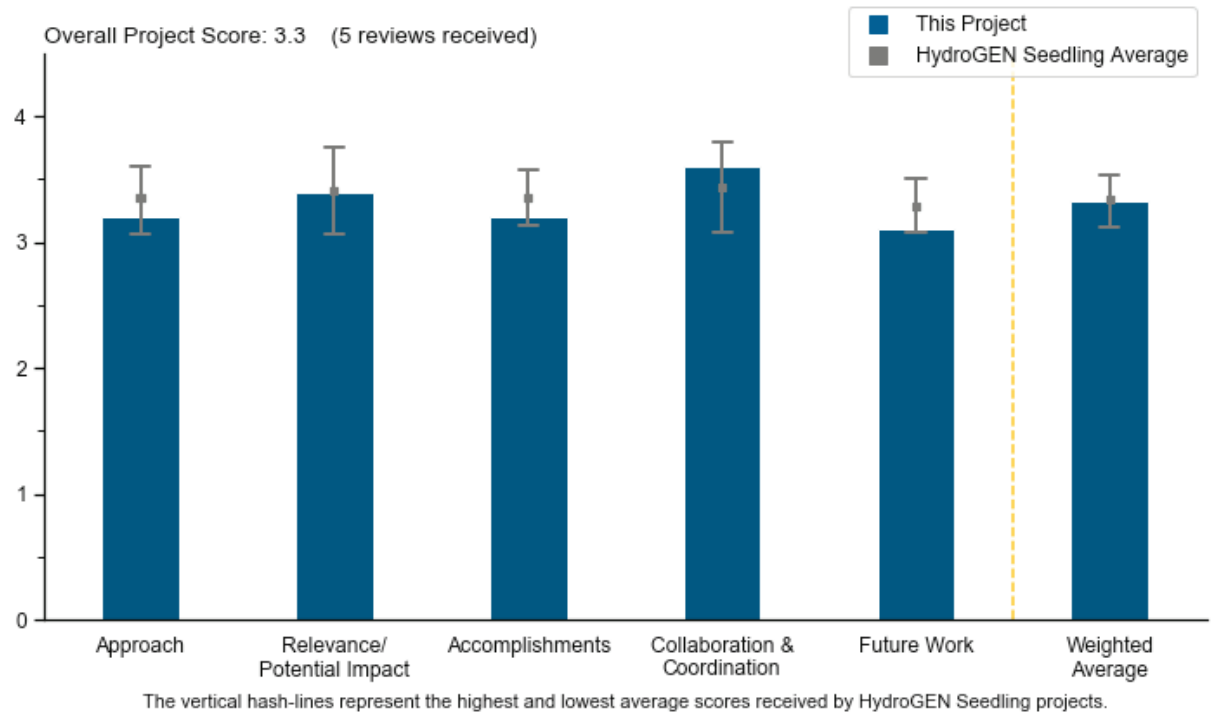
Project #P-160: Best-in-Class Platinum-Group-Metal-Free Catalyst Integrated Tandem Junction Photoelectrochemical Water-Splitting Devices

Charles Dismukes, Rutgers University

Brief Summary of Project

This project will identify the best technical approaches to fabricate both high-performance (HP) and high-value (HV) platinum-group-metal-free (PGM-free) catalysts for photoelectrochemical (PEC) cells without compromising system efficiency. Next-generation devices must eliminate PGMs, even though they perform well, because of cost and sustainability limitations. Using recently developed low-cost HP catalysts, the team will examine the optimal pairing of these materials with established HP and emerging HV photoabsorbers. Cost–benefit analysis of full HP and HV devices and their individual components will enable the preparation of a hybrid product that will significantly advance the state of the art and that has the potential to deliver on all U.S. Department of Energy figures of merit: cost, performance, and stability.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.2** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The focus on demonstrating improvements to an HP and HV integrated system is a well-conceived plan. The developed designs show a nice synergy between node capabilities and local expertise. Much of the effort to date has focused on the integration of components, and now with demonstrated success here and as the project further matures, it may be useful for the group to think strategically about how to improve both efficiency and durability. This is true in particular with respect to durability; the group should think about how they intend to understand the limiting features and overcome them. A clearer strategy here for the HP and new HV system may be warranted.
- The team has proposed an approach that explores two potential systems: an HP device based on III–V semiconductors and an HV one that uses inexpensive light absorbers. The approach leverages novel

electrocatalysts developed at Rutgers University (Rutgers) and looks at how they may be integrated through interfacial and protective layers with light absorbers. The HP devices are aligned with possibly reaching the DOE performance targets of 20% solar-to-hydrogen (STH) efficiency, and the HV with the $2/kg cost goal. Although these two systems may seem reasonable, it is unlikely that any of the systems would satisfy both performance metrics. The approach for the development and integration of protective coatings and electrocatalysts is appropriate, and the principal investigator (PI) has a proven track record with the materials proposed. The project is well integrated with the HydroGEN network, and the team effectively leverages HydroGEN resources that have complemented project developments. This includes partnerships with the National Renewable Energy Laboratory (NREL) for light absorber development and on-sun testing. The approach to developing HV devices involves the exploration of multiple possible light absorbers but lacks a clear rationale for the choice of materials. The hybrid organic–inorganic perovskites (HOIPs) system demonstrated is quite promising in terms of efficiency and cost, but it needs to be encapsulated to withstand being submerged in electrolyte. It seems clear that a photovoltaic (PV) electrolysis approach is more appropriate to this system.

- Developments utilizing $LiCoO_2$ oxygen evolution reaction, Ni_5P_4 hydrogen evolution reaction, and a TiN diffusion barrier are notable and may have good promise.
- There is a good balance to proving low-cost catalysts can operate in these PEC system configurations on high-cost/HP devices while simultaneously trying to develop them in inexpensive systems.
- The project's approach is effectively addressing the important issue of finding a balance between performance, durability, and cost.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- This project shows a very nice synergy between the participants (i.e., NREL III–V nitrides and Rutgers' work in PGM-free catalysts) in the demonstration of new PEC devices. The new device architectures do have good potential to advance the field. Although much of the focus has necessarily been on integration thus far, there are already promising results. As the project continues to mature, to maximize this impact, it will be necessary to identify techniques for improving efficiency and durability. The team has suggested several routes for the former, but the latter appears somewhat less well developed. While durability is a very challenging problem, it will be necessary to identify strategies to understand and mitigate degradation in the project systems if maximum impact is to be realized.
- The project supports and advances progress toward DOE Hydrogen and Fuel Cells Program (the Program) goals and objectives and also supports the HydroGEN Consortium mission. The HP thrust is making progress toward the DOE's technical targets for PEC efficiency and stability, while the HV approach is attempting to address costs. There is good leverage of HydroGEN resources available to the project.
- The project partly supports the DOE hydrogen goals, as it provides a path for the development of either high-efficiency STH electrodes that are stable for prolonged periods of time or HV devices that may produce hydrogen at a reduced cost. The project also enhances the HydroGEN network, as the team may be able to provide a protocol for the synthesis of high-efficiency electrocatalysts, which may be leveraged by others in the PEC community, thus leading to integrated PEC systems with earth-abundant electrocatalysts. It is unlikely that the project will have a direct impact on the $2/kg DOE goal, given the significant barriers: (1) the III–V-based photoelectrodes explored in the HP devices are too costly, and (2) the HV devices have very limited efficiencies (perhaps with the exception of the HOIP system).
- Achieving the three factors of efficiency, durability, and cost is crucial for reaching the DOE goal of $2/kg of hydrogen. Therefore, this project is very relevant, and the potential impact is high.
- The project's relevance and potential impact is satisfactory.

Question 3: Accomplishments and progress

This project was rated **3.2** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The team has shown adequate progress toward meeting most of the targets. The $LiCoO_2/ZnSnN_2$ photoanode work is not complete. The team has made good progress toward the integration of NiP_2 electrocatalysts with HP photoabsorbers. The achievement of HP devices capable of performing unassisted water-splitting at an STH efficiency of 11.5% is promising, but it is still far from the 20% STH required by the Program. The durability tests on a $Ni_5P_4/TiN/GaInP_2$ device are encouraging, but the fact that the photoelectrodes needed to be periodically etched to sustain activity is concerning. The team was able to rapidly evaluate $ZnSnN_2$ light absorbers and discard this materials system because of its poor performance. The incorporation of HOIP light absorbers with high efficiency can lead to high-efficiency HV devices and thus should continue to be explored. Although the quality of the $SrNbO_2N$ films obtained is high, their performance is quite low, and thus continuing to explore them seems unjustified.
- The go/no-go metrics were fairly aggressive, and NREL validated the data gathered at Rutgers. The accomplishments in the HP thrust are outstanding, but the HV is showing only fair progress. It was a good choice to move on from the $ZnSnN_2$ material that was not showing any promise. The $SrNbO_2N$ should either quickly show it can achieve several mA/cm^2 or be abandoned. It was a prudent move to include the HOIPs node to bring into this project some low-cost materials that have the potential to generate photocurrent and photovoltage.
- The project has made substantial progress in the HP system, having met the targets for both efficiency and durability. The decision to forgo the nitride system and move toward an alternative HV structure, taking advantage of node capabilities, is reasonable.
- Overall, the project team has achieved great accomplishments. If they were successful in making the low-cost approach with $ZnSnN_2$ work, the score would have been higher. However, given the limited resources, the team made the right decision in discontinuing this subtask.

Question 4: Collaboration effectiveness

This project was rated **3.6** for its collaboration and coordination with HydroGEN and other research entities.

- This is a highly collaborative effort, which has benefitted from several node capabilities in metal–organic vapor-phase epitaxy (MOVPE), III-V semiconductor & semiconductor characterization (referred to as the PEC node in the presentation), High-Throughput Experimental Thin Film Combinatorial Capabilities (referred to as the HTE node in the presentation), and HOIPs. There are strong, demonstrated interactions with nodes, participation in HydroGEN activities, and contributions to HydroGEN's Data Hub.
- The project shows close, appropriate collaboration with other institutions, specifically the HydroGEN Consortium, with appropriate use of nodes, contributions to the benchmarking and protocols (2b) project, and the HydroGEN Data Hub. The project's partners are full participants and well coordinated. There is evidence of significant interaction and collaboration.
- There are good collaborations within the team, as well as with the capability nodes, that are clearly well reflected in their accomplishments.
- The project team shows good collaboration with NREL.
- The team effectively leverages nodes at NREL that directly enhance the project activities.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The project's proposed future work is on a good track.
- The project's proposed future work is generally effective but could be improved; it contributes to overcoming some barriers, meeting some end-of-project goals, and potentially to advancing the materials research mission of the HydroGEN Consortium. The HP targets and tasks are outstanding. Focusing on short-circuit stability testing, pushing on efficiency with next-generation III–V tandems, and validating

both with on-sun testing is precisely what this project should be focusing on to meet DOE technical targets. The future work for the HV is only fair because of the partial focus on exploratory materials that have yet to prove their worth (e.g., $SrNbO_2N$), which is partially abated by the perovskite work.

- Focusing on improving the performance of HP III–V devices seems appropriate, especially given that only 11.5% STH has been demonstrated. The on-sun testing seems premature, especially given that the efficiency targets have not been met. Spending valuable resources on understanding the behavior of under-optimized photoelectrodes under real-world conditions seems unjustified. The team should consider demonstrating a device with a ~>20% STH target before engaging with the on-sun testing. Continuing to work on p-$SrNbO_2N$ photoabsorbers also seems unjustified, given that the current densities obtained were less than 500 uA/cm^2. The team might benefit from investing the resources granted toward HOIP devices, which are significantly more promising.
- The proposed future work seems reasonable but is vague in many instances. For the HP device, there are proposed approaches to improving the efficiency, but more clarity on understanding degradation and improving durability would be beneficial. Regarding the new HV system, the goals are still focused on demonstrating half-cells with the alternative anode materials, but if this can be accomplished, then it is unclear what the associated targets are for efficiency and durability.
- Dropping the least promising subtask is making the proposed future work more promising, with more focus and concentrated effort.

Project strengths:

- This project is making remarkable progress in the HP thrust, with a low-cost catalyst that has shown protective abilities in addition to being an excellent hydrogen evolution catalyst. The interaction with the rest of the HydroGEN nodes and 2b team is another notable strength.
- The project team has demonstrated integration of Ni_5P_4/TiN with $GaInP_2$, reached >10% STH with HP devices, and rapidly screened $ZnSnN_2$ properties, concluding that it had no promising performance properties.
- This is a very competent team, fully leveraging their assets of non-PGM catalysts and surface coating. The very effective collaborations are clearly reflected in their very successful accomplishments.
- The key strengths of this project are the unique device designs that combine expertise of all participants, the strong interaction with nodes, and the focus on demonstration of both an HP and HV device.
- The project team has identified a promising HV device based on HOIP photoabsorbers.
- The project's strengths include the use of new materials.

Project weaknesses:

- There are not many weaknesses. If there was one, it was that not much attention seemed to be paid to understanding why $ZnSnN_2$ did not perform well. However, presumably it was a strategic choice to save resources.
- It is not clear whether the device will work if the pinholes during manufacturing are not avoided. This may indicate a design that is not robust.
- The project's efficiency levels are far from DOE targets, and there is not a clear path to achieving them. Continuing the work on $SrNbO_2N$ is unreasonable based on the poor performance of this photoabsorber. On-sun testing is premature, given the lack of high-efficiency PEC materials.
- The project's largest weakness may be the lack of clarity on strategies for understanding degradation mechanisms and improving durability in the fabricated devices.
- Little progress has been made in the HV thrust.

Recommendations for additions/deletions to project scope:

- The team should consider focusing all their efforts on the most promising HV material, HOIP. For the HP materials, a clear set of tasks and a timeline should be defined to reach the 20% STH target set by DOE.
- Completion of the proposed work is strongly recommended.
- The scope of the project seems reasonable.

- The HV thrust that relies on the HTE node should be re-scoped. While the HTE node might be an appropriate tool for validating theoretical predictions of physical properties of a combination of various elements, to date it has been unable to provide a material that could reasonably be called a photoelectrode.

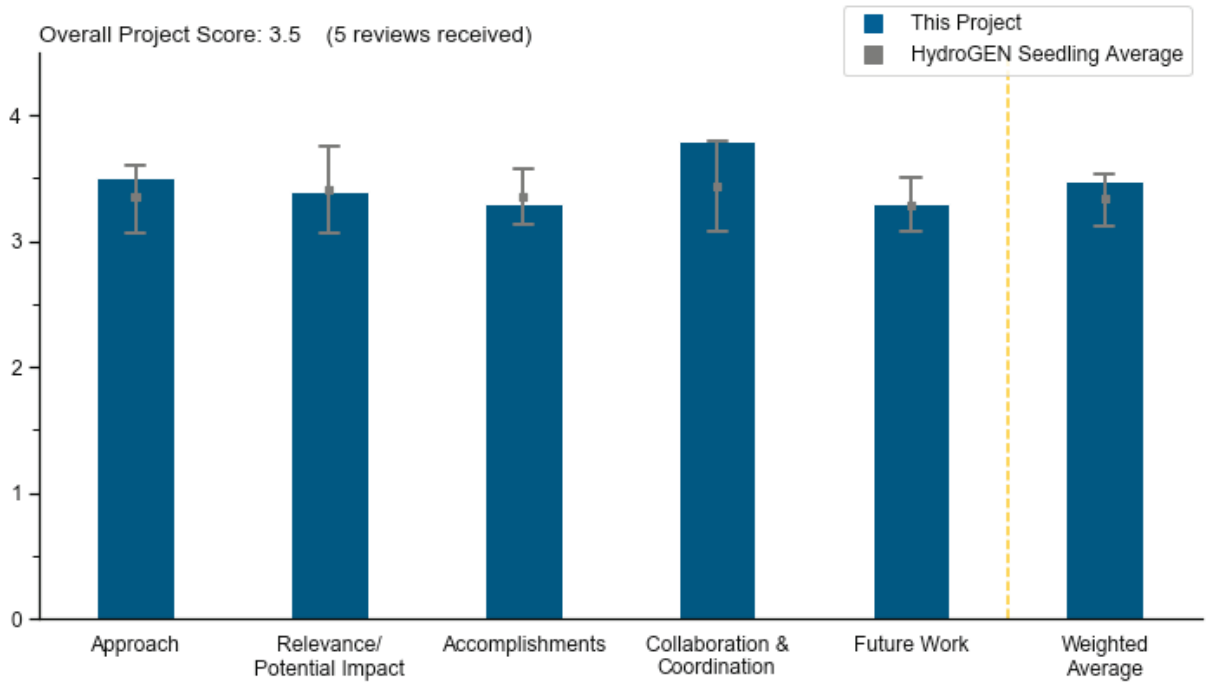
Project #P-161: Protective Catalyst Systems on III-V and Silicon-Based Semiconductors for Efficient, Durable Photoelectrochemical Water-Splitting Devices

Thomas Jaramillo, Stanford University

Brief Summary of Project

The overall goal of this project is to develop unassisted water-splitting devices based on III-V materials, creating pathways to improve performance in terms of efficiency (>20% solar-to-hydrogen [STH]), durability (two weeks), and cost (<$200/m^2). Two distinct water-splitting schemes are being pursued: Scheme 1 (tandem III-V/III-V) aims to develop high-efficiency devices with tandem III-V photoabsorbers (e.g., $GaInP_2$/GaInAs), and Scheme 2 (III-V/Si) targets cost reduction while maintaining high efficiency by growing InGaN on crystalline Si. Both schemes will be coupled with thin-film, semi-transparent hydrogen and oxygen evolution reaction catalytic/ protection layers containing reduced or zero precious metal content that can enhance durability while maintaining high efficiency and enabling low material costs.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.5** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The approach is sharply focused on critical barriers and validating technology innovation and is difficult to improve significantly. The barriers have been clearly identified and are being addressed through project innovation. It is a well-designed project that is highly integrated with the HydroGEN Consortium network. The budget period 1 work scope was used to validate the approach and technology innovation.
- The principal investigator has proposed Scheme 1 using III-V/III-V and Scheme 2 using III-V/Si to overcome the barriers. This dual approach is excellent, as the first one aims for the high-efficiency devices and the second one for utilizing existing Si-based technologies.

- The team has proposed an approach that combines the development of high-efficiency III-V photoelectrodes and earth-abundant, protective electrocatalytic coatings to reach a >20% STH that is stable for prolonged periods of time. This is in line with U.S. Department of Energy (DOE) desired targets for photoelectrochemical (PEC) devices.
    - The approach for the development of protective coatings is appropriate, and the principal investigator has a proven track record with the system proposed. Preliminary results are encouraging, although the protective layers ultimately degrade in a limited number of hours.
    - The fundamental approach proposed to understand degradation is likely to lead to useful insights that may assist in the development of more stable protective coatings. Despite the need for such fundamental studies, it is likely that the time required to understand degradation mechanisms will go beyond the timeframe of the current project. Thus it is unlikely that the project will have a significant impact on the ultimate objective of the DOE Hydrogen and Fuel Cells Program (the Program), independently of the project's self-evident scientific merits in the context of the broader PEC community.
    - While focusing on III-V semiconductors is reasonable in the context of the STH efficiency target, it is difficult to justify that the $2/kg goal can be achieved with the current approach. The team's approach to this economic target is to develop III-V/Si tandems, but the potential cost benefits of such an approach are not quantitatively addressed to fairly evaluate the validity of the approach.
    - The project is well integrated with the HydroGEN Consortium network, and the team effectively leverages resources from it that have complemented project developments.
- This is a well-designed project that targets ambitious PEC goals of demonstrating 20% STH, with on-sun testing for two weeks, via incorporation of protective catalysts on III-V systems. The use of these transition metal-based catalysts on III-V- (and Si-) based systems offers a promising route forward on a challenging problem. The team is pursuing a few device structures in parallel, with the ultimate goal of demonstrating a Si/InGaN system that achieves these goals. The utilization of Energy Materials Network (EMN) capabilities and collaborations is strong as well.
    - Most of the project objectives are concrete (e.g., unassisted water-splitting devices that can achieve >20% STH efficiency and operate on-sun for at least two weeks). However, the objective to provide a path toward electrodes that cost $200/m^2 via earth-abundant, protective catalysts and novel epitaxial growth schemes is not. It is not clear what constitutes "providing a path."
    - The part of the approach that seems the least well developed is the in operando characterization for in-laboratory stability studies. This is an admittedly challenging problem, and the research community certainly stands to learn a good deal from these measurements. However, what is less clear is, even if specific degradation modes are identified, what can be realistically done over the project time frame to overcome limitations.
- Overall, the approach is well-balanced, addressing efficiency, durability, and cost. One minor comment is that MoS_2-based surface protection has a disadvantage in achieving surface protection and catalytic activity simultaneously because of the edge active nature of the material as a catalyst.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- There are strong potential impacts in (1) the demonstration of stabilization of III-V surfaces via earth-abundant, protective catalysts, (2) the potential offered by the InGaN/Si device, which, if successful, may offer a path to high efficiencies with inexpensive processing, and (3) the plans for multiple-week on-sun testing. The team is making substantial progress toward the ultimate project goals, and whether they are ultimately met or not, the project will help us to learn many new things.
- The project aligns well with the Program and DOE research, development, and demonstration (RD&D) objectives, has the potential to advance progress toward DOE RD&D goals and objectives, and is aptly leveraging and contributing to the resources and framework of the HydroGEN Consortium. The varied tasks appropriately address the most important performance metrics of the PEC system, namely efficiency, durability, and cost. For example, working on a transferrable, protective catalytic coating on an efficient but too costly III-V that could eventually be applied to the low-cost InGaN/Si system is an effective way of parallelizing the research activities to ensure continued progress.

- This project addresses the crucial factors for the DOE goal, achieving efficiency, durability, and cost simultaneously. Therefore, it is very relevant, and the potential impact is very high.
- The project supports the Program goals as it provides a path for the development of high-STH-efficiency electrodes that are stable for prolonged periods of time and produce hydrogen at a reduced cost. The project also enhances the HydroGEN Consortium network, as the team may be able to provide a protocol for the synthesis of high-quality, protective electrocatalytic coatings to other teams in the network and synergistically accelerate a path toward more stable PEC devices.
    - It is unlikely that the project will have direct impact on the $2/kg DOE goal, given significant barriers to obtain (1) III-V-based photoelectrodes with significantly reduced costs to outcompete alternative technologies such as Si-based photovoltaic-driven electrolysis, or (2) a high enough STH to offset the higher cost from the III-V semiconductors. The team is far from the 20% STH target, and even if this is reached, it is not clear how this may offset the high cost from III-V semiconductors.
- The work directly supports the Program goals.

Question 3: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project is effective, contributes to overcoming most barriers, and provides data that considerably supports the accomplishments toward impactful go/no-go criteria. The durability results are impressive for a III-V photocathode, and progress toward the go/no-go criteria is supported by unambiguous data.
- The accomplishments to date are impressive overall, with project milestones met or very nearly met. If the InGaN/Si device is the ultimate target for efficient, durable, and low-cost PEC devices, then there are still several steps to be taken to achieve project goals in this structure. At present, the team is still working on demonstrating rectifying behavior in this system and will strategically need to move toward PEC devices and assessment of efficiency and durability.
- The team has made good progress toward developing Scheme 1 and 2 photoelectrodes, protective coatings, and analytical techniques to assess degradation mechanisms.
    - The achievement of >5% STH unassisted water-splitting devices was aligned with the initial targets, but these devices were based on Scheme 1 photoelectrodes, which are expected to be significantly more expensive than Scheme 2 photoelectrodes. Also, the operation of these photoelectrodes was sustained for only a limited number of hours, and it is unclear how long-term stability may be achieved.
    - The STH achieved initially is far from the project target of 20%, and despite trying different material systems, no significant breakthrough has been reached.
    - The preliminary plans and results on the in situ flow cell for Raman microscopy are encouraging for better understanding of degradation mechanisms.
- Progress on most of the important tasks is on track, steadily moving toward the DOE goals. One minor comment is that the progress in improving the durability is slightly lagging behind the rival approach. It is hoped that this is not due to the choice of protection scheme.
- The team is making adequate progress toward the goals. Unassisted water splitting is showing improvement but is far from the PEC goal.

Question 4: Collaboration effectiveness

This project was rated **3.8** for its collaboration and coordination with HydroGEN and other research entities.

- The project has close, appropriate collaboration with other institutions, specifically the HydroGEN Consortium, with appropriate use of nodes, contributions to the benchmarking/protocols (2b) project, and the HydroGEN Data Hub. Partners are full participants and well coordinated. There is evidence of strong coordination with the HydroGEN nodes, as well as the 2b project. There appears to be regular, meaningful interactions between this project and the nodes.

- The team effectively leverages nodes at Lawrence Berkeley National Laboratory (LBNL) and National Renewable Energy Laboratory, which directly enhances the activities of the projects. The new collaboration with LBNL for the in situ Raman spectroscopy is well suited.
- The team demonstrated very well-coordinated efforts that are evidenced in robust progress in improving the efficiency and durability of three types of devices based on III-V and nitride.
- The effort synergizes nicely with EMN nodes and capabilities, which are integrated throughout most tasks on semiconductor epi-layer fabrication and characterization, corrosion analysis, and on-sun benchmarking.
- The project has excellent collaboration.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The incorporation of in situ Raman surface observations is an appropriate path to enhancing the understanding of corrosion phenomena. Also, the use of on-sun testing is important to translate the performance under the artificial conditions applied in the laboratory to a more meaningful and relevant set of conditions an actual PEC device would encounter.
- Given the steady progress made toward DOE goals, continuing the current tasks with an additional in operando corrosion study seems a rational choice.
- The principal investigator has clearly identified the remaining challenges and barriers. The mechanistic understanding of the stability will be of value to the research community.
- A specific set of tasks that will be explored for the optimization of Scheme 1 and 2 photoelectrodes were missing from the presentation. This is particularly important because the performance of the devices tested to date is far from the project target, and the time and financial resources to achieve the required improvements are very limited. A more specific set of tasks and a timeline for research and development activities that directly tackle the pain points of the tested devices would be useful at accelerating the path toward a high-efficiency device. The proposed in situ characterization work is well aligned with the objective of improving the stability of these devices. The on-sun testing seems premature, especially given that the efficiency targets have not been met. Spending valuable resources on understanding the behavior of under-optimized photoelectrodes under real-world conditions seems unjustified.
- The future work as presented was somewhat vague. A fair number of steps remain ahead to achieve the ultimate goal of 20% STH efficiency, and the specific barriers and next steps to overcome these barriers were not clearly outlined.

Project strengths:

- There is a strategic focus on goals and the potential to make a fair amount of headway in (1) stabilization of III-V surfaces via protective catalysts, (2) fabrication of InGaN/Si tandem, and (3) collection of on-sun data via collaboration with EMN nodes.
- All of the personnel, from the principal investigator to the graduate students, are highly skilled and knowledgeable in materials synthesis, characterization, and PEC water-splitting phenomena. The intellectual rigor they apply to the project is obvious.
- The project has demonstrated protective electrocatalytic coatings with long-term stability, as well as >10% STH PEC devices based on III-V tandem electrodes. There is strong integration with the HydroGEN Consortium network and collaborations among team members. There is a clear path to identify degradation mechanisms through in situ spectroscopy.
- The principal investigator has been demonstrating the leading role in the PEC community with extraordinary scientific contributions, and this team is showing itself to be a role model for the HydroGEN Seedling projects by being engaged in the great collaborations.
- The strong team is the strength of this project.

Project weaknesses:

- It is difficult to find a weakness. If any, the late introduction of the in operando corrosion study may delay development of a mitigation strategy.

- The only weakness of the project is the slow progress the InGaN/Si task seems to be making. There is not much time left in the project to prove a tandem structure can split water spontaneously and then to optimize the performance.
- STH achieved in Scheme 1 devices is far from the project target, and a clear path to efficiency improvements has not been presented. On-sun testing is premature, given the lack of a high-efficiency PEC materials system.
- A clear path to improved performance, particularly with respect to durability, will need to be identified.

Recommendations for additions/deletions to project scope:

- This project has shown very robust progress toward the DOE goals, and the principal investigator continues to contribute to the PEC research community. The continuation of the proposed work is strongly supported. The in operando corrosion study should be given higher priority to accelerate development of an effective protection method.
- The team could leverage Si/InGaN tandems developed by other HydroGEN teams to surpass one of the project's technical milestones without spending resources to develop an alternative fabrication approach for an equivalent materials system.
- The project scope is reasonable as is.

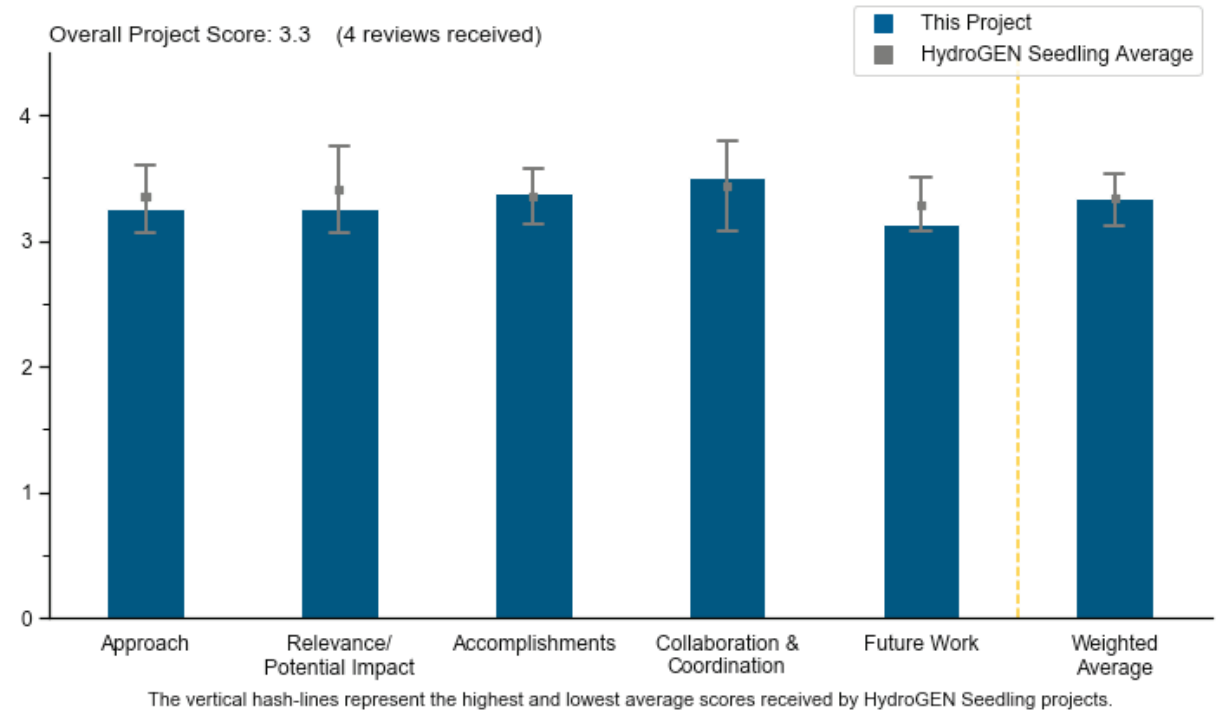
Project #P-162: Novel Chalcopyrites for Advanced Photoelectrochemical Water Splitting

Nicolas Gaillard, University of Hawaii

Brief Summary of Project

The overarching goal of this project is to create a chalcopyrite-based, semi-monolithic, tandem hybrid photoelectrode device prototype that can operate for at least 1,000 hours with solar-to-hydrogen (STH) efficiency >10%. The performance of previously identified wide-bandgap chalcopyrite materials will be improved through alkali doping to passivate copper indium gallium selenide (CIGS) defects, and next-generation chalcopyrites (e.g., Ga-free) will be developed. The photoelectrochemical (PEC)–electrolyte interface energetics and stability will be improved by investigating alternative buffer materials and protective layers. Also, novel fabrication methods will be developed for creating the semi-monolithic chalcopyrite-based tandem devices.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.3** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- This project targets the development of chalcopyrite-based PEC tandem devices that are inexpensively manufactured via solution processing and bonding techniques. The ultimate goals are listed as achieving improvements in STH efficiency from 4% to 10% and improvements in durability from 350 hours to over 1,000 hours. There is a clear vision, a target device design, and a set of objectives that must be met to achieve the goals. A potential concern may be that for the most part, the initial set of milestones focuses to a large extent on proof-of-concept demonstrations for more well-studied materials, rather than the new chalcopyrite materials targeted by the effort. The efforts working with the new chalcopyrites appear to be relatively new, and as such, many of the critical goals of this project are backloaded, coming toward the end of the project. There may be several issues to overcome once the team turns to the new widegap and

interface materials systems of interest, especially once the project moves toward PEC devices and the characterization of their performance.

- The team's approach thoroughly explores the implementation of chalcopyrite-based PEC systems by combining experimental and synthesis methods for chalcopyrite photovoltaics (PV), with tandem device integration through transparent interfacial layers and protective catalytic coatings to enhance stability. Printable chalcopyrites are interesting from an economic perspective, as they may lead to low-cost PEC materials. In terms of efficiency, it is unlikely that the chalcopyrites explored are capable of reaching the U.S. Department of Energy goal of 20% STH efficiency. The approach is missing a clearly articulated path to reach high efficiency. The team is well integrated and leverages complementary expertise from principal investigators (PIs) from multiple universities and HydroGEN nodes.
- The project's approach is effective and contributes to overcoming most barriers and validating technology innovation. The PI has identified four key barriers and is addressing each of them through innovative approaches. It is a well-designed project and is integrated into the HydroGEN network.
- Chalcopyrites have shown great promise in PV. The project explores its PEC applications. The project team has planned adequate tasks related to synthesis, interface engineering, and device integration. The proposed "printing" technique can help realize the cost targets.

Question 2: Relevance/potential impact

This project was rated **3.3** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- Most of the project aspects align with the DOE Hydrogen and Fuel Cells Program (the Program) and DOE research, development, and demonstration objectives, and the project is adequately leveraging and contributing to the resources and framework of the HydroGEN consortium. The strength of the project is exploring the materials space of the chalcopyrites and investigating novel, lower-cost synthesis approaches to these materials that can generate high current densities. Unfortunately, these materials continue to struggle in generating a sufficient photovoltage in a PEC configuration, which makes them unlikely to meet the STH efficiency target. Another weakness is that these appear to be economical only under very high solar concentrations (25x), which is an unlikely scenario for a functional device because of mass transport issues under concentration.
- From the technoeconomic standpoint, there is high potential impact, should the project be successful. This is especially true if it turns out that it is possible to inexpensively print the widegap chalcopyrite materials and use the proposed exfoliation and bonding approach to build a multijunction device. These goals are fairly ambitious, but even demonstrating progress on individual technical barriers (even if ultimately they cannot all be overcome) will offer valuable steps forward for PEC water splitting.
- The project partly supports the Program's goals, as the exploration of inexpensive, printable chalcopyrite materials may lower the cost of PEC materials, but it is unlikely to match the efficiency targets required. The materials presented have demonstrated a PV efficiency of only ~10%, which is anticipated to drop when integrated into a PEC device. The project also enhances the HydroGEN network, as the team may be able to provide new light absorbers, which may be integrated in PEC devices with multiple components from the community.
- The potential impact of the work is high owing to the possible compatibility with industrial manufacturing.

Question 3: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project has met its milestones for the first year and is currently working toward second-year milestones. The group has successfully identified alternative chalcopyrite materials ($Cu(InAl)Se_2$, $Cu(InB)Se_2$) that may exhibit fewer defects during synthesis or manufacturing, but the group now needs to turn the focus to demonstrating the printing of the new materials. Similarly, the group has successfully demonstrated the exfoliation and bonding approach for more standard materials (e.g., CIGS) but will need to start developing this for the new materials of interest.

- The project has been effective; it contributes to overcoming most barriers and provides data that considerably support the accomplishments toward impactful go/no-go criteria. There has been considerable progress in this project on many fronts, despite the lack of a single, high-efficiency PEC device. The accomplishments on modeling, ink printing, surface treatments, and transparent conductive binders are significant and could be applied to other material systems if the current set is unable to meet PEC water-splitting targets.
- The team has shown promising integration of modeling with synthesis activities in the context of chalcopyrite PV. The transparent conductive binders show promising performance, both in terms of their optical properties and their electrical conductivity, and these materials may be leveraged for other energy applications. The WO_3/Pt protective layer shows reasonable performance over hundreds of hours, although the performance progressively degraded over time.
- The team is making adequate progress toward the goals.

Question 4: Collaboration effectiveness

This project was rated **3.5** for its collaboration and coordination with HydroGEN and other research entities.

- There is close, appropriate collaboration with other institutions, specifically HydroGEN, with appropriate use of nodes, contributions to the benchmarking and protocols (2b) project, and the HydroGEN Data Hub. The project's partners are full participants and well coordinated. This project is very well integrated with external collaborators (including the University of Nevada, Las Vegas, and Stanford University) in addition to HydroGEN nodes and the 2b team.
- Several collaborations with Energy Materials Network (EMN) nodes are detailed. While some of these seem critical to the project itself, the specific synergies with other collaborations were somewhat less clear. For example, combinatorial development of tunable buffers to improve the interfacial properties supports a critical goal of this project, which is to improve interface stability and performance in the integrated systems. On the other hand, it was less clear how some aspects of the theory and modeling results are to be integrated into the future work and help with specific programmatic goals.
- The team leverages effectively nodes at Lawrence Berkeley National Laboratory, the National Renewable Energy Laboratory, and Lawrence Livermore National Laboratory, which directly enhances the activities of the projects.
- There is good collaboration with the EMN node experts.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The project's proposed future work is effective; it contributes to overcoming most barriers, meeting most end-of-project goals, and advancing the materials research mission of HydroGEN. The tasks of modeling, interface engineering, and hybrid device integration will likely continue to make good progress over a broad scope of PEC-related areas. There should be some emphasis placed on making actual devices that can perform unassisted water splitting.
- The planned future work is a logical continuation of ongoing efforts, and it is good that the group will move toward working with the widegap alkaline chalcopyrite materials. If the group wishes to demonstrate a more efficient, more durable chalcopyrite tandem-based PEC device by the end of the project, it may be strategic to push on PEC devices and the actual production of hydrogen sooner rather than later.
- The proposed subtasks in task 1 are not directly aligned with developing a material capable of achieving 20% STH efficiency. It would be useful to explicitly describe a path for chalcopyrites to reach that level of efficiency and align tasks in that path. On task 2, it is clear that the WO_3 protective layers need improvements, but it is also unclear whether the team has a well-defined path to achieving those improvements. The future work on task 3 seems well aligned with the ultimate project goal of developing monolithic devices, and thus it is appropriate.
- The proposed tasks are in line with solving remaining barriers.

Project strengths:

- The strengths of the project include its clear vision for an inexpensive chalcopyrite tandem PEC device, with a good deal of attention being paid to achieving manufacturability via low-cost printing and exfoliation and bonding approaches.
- The project has demonstrated a good match between theoretical calculations and synthesis, a robust synthesis method for chalcopyrites, and promising transparent conductive binders.
- The project's strengths include the possible use of "print" technology to make the electrodes.
- The PI and assembled team are highly competent and are making excellent progress by integrating theory, synthesis, and characterization.

Project weaknesses:

- The efforts working with the newer material systems appear to be relatively new, and as such, many of the critical goals of this project are backloaded. There may be several issues to overcome once the PIs turn to the new widegap and interface materials systems of interest, especially once the project moves toward PEC devices and the characterization of their performance.
- The protective coatings degrade continuously over time; better understanding on the degradation mechanisms is needed. There is no direct path for achieving DOE target STH efficiency.
- A major weakness of the approach is the poor stability of the elements used in the electrode. For example, Cu is very easily degraded and leached out by water.
- The chalcopyrite materials set has yet to be incorporated into a device that demonstrates unassisted water splitting.

Recommendations for additions/deletions to project scope:

- The project team should envision a faster path toward a monolithically integrated device with maximum achievable efficiency. The team should perform detailed technoeconomic analysis on that design.

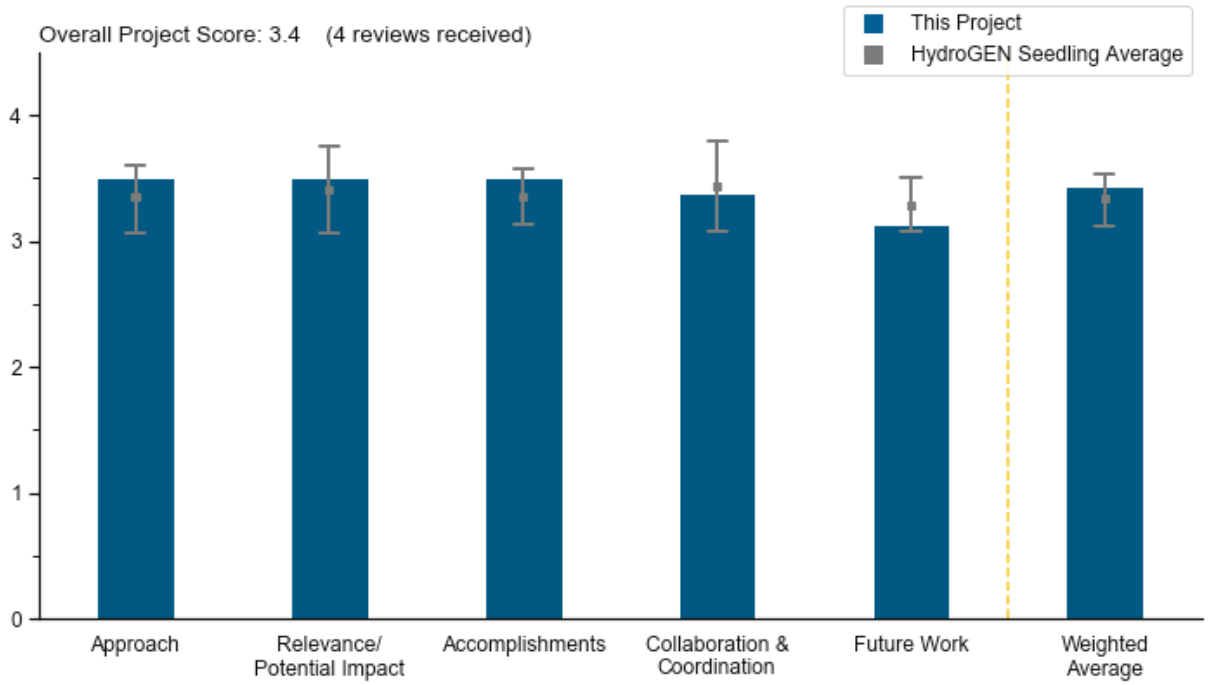
Project #P-163: Monolithically Integrated Thin-Film/Silicon Tandem Photoelectrodes for High-Efficiency and Stable Photoelectrochemical Water Splitting

Zetian Mi, University of Michigan

Brief Summary of Project

This project seeks to establish a low-cost and scalable platform for high-efficiency and stable photoelectrochemical (PEC) water-splitting devices and systems. The improved performance of the top photoelectrodes is required to realize high-efficiency, unassisted solar water splitting, and a functional wide-bandgap tunnel junction that can be fabricated on a silicon platform is a critical component of a silicon-based tandem solar water-splitting device. The tandem photoelectrodes being developed in this project use silicon as the bottom light absorber and newly developed low-cost photoelectrodes made of Ta_3N_5, BCTSSe, or InGaN as the top light absorber. As silicon and gallium nitride are the two most produced semiconductors, the technology being developed will be scalable and lend itself to low-cost manufacturing.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.5** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The team has clearly identified a target of high potential impact. The approach to reliably generate Si/GaN-based tandem photoelectrodes has the potential to lead to high solar-to-hydrogen (STH) while, at the same time, lowering the manufacturing cost of photoelectrodes.
    - The protection strategy for the photoelectrode seems appropriate, and its implementation is relatively straightforward. Results on N-terminated GaN electrodes are encouraging.
    - Growing high-efficiency GaN directly on Si has the potential to significantly lower the cost of III-V photoelectrodes.

  - The project is well integrated with the HydroGEN Consortium network, and the team effectively leverages resources from it, which have complemented the developments of the project.
  - Integration of co-catalysts could have a big impact in the performance of the ultimate devices. This can be done either through collaborations in the HydroGEN Consortium network or with other projects in the program. This could help further enhance the stability of the photoelectrodes and ultimately lower the overpotentials required for water splitting.
- This project is focused on developing Si/InGaN tandem photoelectrodes that exhibit 10% STH efficiency and 1,000 hours of operation. There is a clearly defined goal and target device design, with appropriate attention paid to manufacturable processing routes. The project vision is built on some potentially promising developments showing stability of N-terminated GaN nanowires (NWs). Overall, this is a worthwhile and potentially impactful effort.
- The approach is effective and contributes to overcoming most barriers and validating technology innovation. The project effectively identifies relevant barriers in durability, device configurations, and synthesis and targets them with innovative approaches. The project is well designed, feasible, and integrated with the HydroGEN Consortium network.
- Barriers of materials durability, device configuration, and manufacturing have been clearly identified. Use of GaN NW tunnel junction on Si is notable, especially the role of Ga-terminated versus N-terminated NWs.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- This project is critical to the DOE Hydrogen and Fuel Cells Program (the Program). It has potential to significantly advance progress toward DOE research, development, and demonstration goals and objectives and is significantly leveraging and contributing to the resources and framework of the HydroGEN Consortium. This material set is extremely promising since it demonstrates high efficiency, durability, and the potential for low-cost synthesis. Using Si as a substrate is game-changing in high-STH-efficiency devices, and if the initial durability results can be extended to 1,000 hours or more, this is a significant advance in PEC water splitting.
- Monolithically integrated Si-based systems offer the potential for low-cost PEC water-splitting systems, and the demonstrated stability of the N-terminated InGaN NW systems is promising. Thus, overall, relevance and impact are high.
- The project has a high potential for the water-splitting community, especially on the search for stable photoelectrodes.
- The project supports the Program goals, as it provides a path for the development of high-STH-efficiency electrodes at a reduced cost. The project also enhances the HydroGEN Consortium network, as the team may be able to provide high-efficiency photoelectrodes to other teams in the network and synergistically accelerate a path toward cost-effective solar hydrogen technologies. However, it is unlikely that the project will have a direct impact on the $2/kg DOE target, given significant barriers to obtain (1) III-V-based photoelectrodes with significantly reduced costs to outcompete alternative technologies such as Si-based photovoltaic (PV)-driven electrolysis, or (2) a high enough STH to offset the higher cost from the III-V semiconductors (the 15% target is not high enough, and there is not a direct path toward achieving higher efficiencies).

Question 3: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The team has made impressive progress toward demonstrating stable GaN-based photoelectrodes, and the robustness of the N-terminated GaN electrodes is an important step toward long-lasting PEC devices. The achievement of 10.5% STH unassisted water-splitting devices based on Si/InGaN is encouraging, and there is clear space for improvements. The results on the efficiency improvements over time are also encouraging

for the long-term stability of the device and may point toward directions to overcome major degradation challenges.

- Progress is effective, contributes to overcoming most barriers, and provides data that considerably support the accomplishments toward impactful go/no-go criteria. Clearly, this project is making progress toward fairly aggressive performance targets. The project has demonstrated a good efficiency with the current device configuration. However, one of the laboratory partners should corroborate the STH efficiency that was a go/no-go metric. Also, two-electrode durability results should be shown to confirm the durability that is inferred by all of the other measurements shown.
- The team has demonstrated InGaN/Si tandem photoelectrodes, and the initial measurements of their stability (300 hours of operation) are promising. Accomplishments to date are good. To move forward from here, it appears that the photoelectrodes' performance (fill factor, current collection) will need to be improved. A clear plan for addressing the current limitations and overcoming limitations was not described in detail.
- The project has shown good progress toward the double-junction photocathode. STH efficiency of 10.5% has been achieved.

Question 4: Collaboration effectiveness

This project was rated **3.5** for its collaboration and coordination with HydroGEN and other research entities.

- The team effectively leverages nodes at Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, and National Renewable Energy Laboratory, which directly enhances the activities of the projects. The collaboration with Francesca Toma is particularly notable, as it can provide insights on novel stabilization mechanisms previously unobserved.
- This project is making good use of Energy Materials Network (EMN) resources, and it is clear that the collaborations are making valuable contributions toward project success. This is particularly true for the in situ PEC scanning tunnel microscopy/atomic force microscopy (STM/AFM) group analysis of degradation during continuous performance, the surface analysis, and band alignment measurements.
- The project has good collaboration, specifically the HydroGEN Consortium, with appropriate use of nodes, contributions to the benchmarking/protocols (2b) project, and the HydroGEN Data Hub. Partners participate and are well coordinated. There is evidence of good collaboration and coordination between the principal investigator and the nodes, as well as good interaction with the 2b project.
- The team has good collaboration with the national laboratories. It will be useful if the collaboration is extended to the industry so the team can benefit from the industrial viewpoints.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The proposed future work is effective and contributes to overcoming most barriers, meeting most end-of-project goals, and advancing the materials research mission of the HydroGEN Consortium. The future work to focus on durability testing of the double-junction electrodes with an STH of >15% has the potential to significantly improve on the state-of-the-art demonstration of high-efficiency and durability if the 1,000-hour target can be met.
- The proposed future work is well laid out.
- The proposed detailed studies on the PEC system are important and will likely lead to relevant physical insights on processes that limit the stability and performance of the photoelectrodes in question. The biggest concern is the lack of a clear path toward the 15% STH device proposed. During the Annual Merit Review presentation, the team indicated several aspects of the project photoelectrodes that needed to be optimized, but a more detailed analysis of the most relevant pain points of the systems and a clear strategy on how to address them were lacking.
- The future work targets focus on PEC studies and on the demonstration of double-junction PEC devices exhibiting >10% efficiency and 1,000 lifetime hours. While this is in line with the overall project goals, the work as presented was very vague. A clear set of remaining barriers to achieving the target efficiencies and stability and a pathway to overcoming these barriers were not laid out.

Project strengths:

- The team's approach and the vision to demonstrate Si-based tandem photoelectrons is solid and may offer a path forward. The early results are promising, including the demonstration of the tandem photoelectrode system that appears to be fairly durable. The use of EMN resources is also excellent, particularly the in situ PEC STM/AFM group analysis of degradation during continuous performance, the surface analysis, and band alignment measurements.
- The team demonstrated a path to reduce the fabrication cost of III-V photoelectrodes, a path to robustly stabilize III-V photoelectrodes, and a >10.5% STH unassisted PEC device. The team has strong integration with the HydroGEN Consortium network and collaborations among team members.
- The team has strong material synthesis skills and good interaction with the HydroGEN nodes.
- An overall strength is the possibility that the team may produce a stable photoelectrode.

Project weaknesses:

- The main weakness may be that, after having demonstrated the Si-based tandem electrode system and making some initial measurements, the specific pathway to overcoming the present performance limitations was not made clear. This makes it difficult to assess the overall likelihood of success in reaching the stated project goals.
- There is an unclear path toward $2/kg, particularly in the context of other solar-hydrogen-competing technologies (PV-driven electrolysis). The project does not define the 15% STH target or the further efficiency improvements needed to meet DOE's ultimate cost and efficiency targets.
- Most of the PEC performance (efficiency, stability) data comes from the principal investigator's laboratory, and it should be validated by one of the DOE partner laboratories.
- The project lacks industrial collaboration.

Recommendations for additions/deletions to project scope:

- The scope of this project is reasonable as laid out.
- The team should consider defining a clear set of tasks and a timeline that will be directly aligned with the project goal of 15% STH.

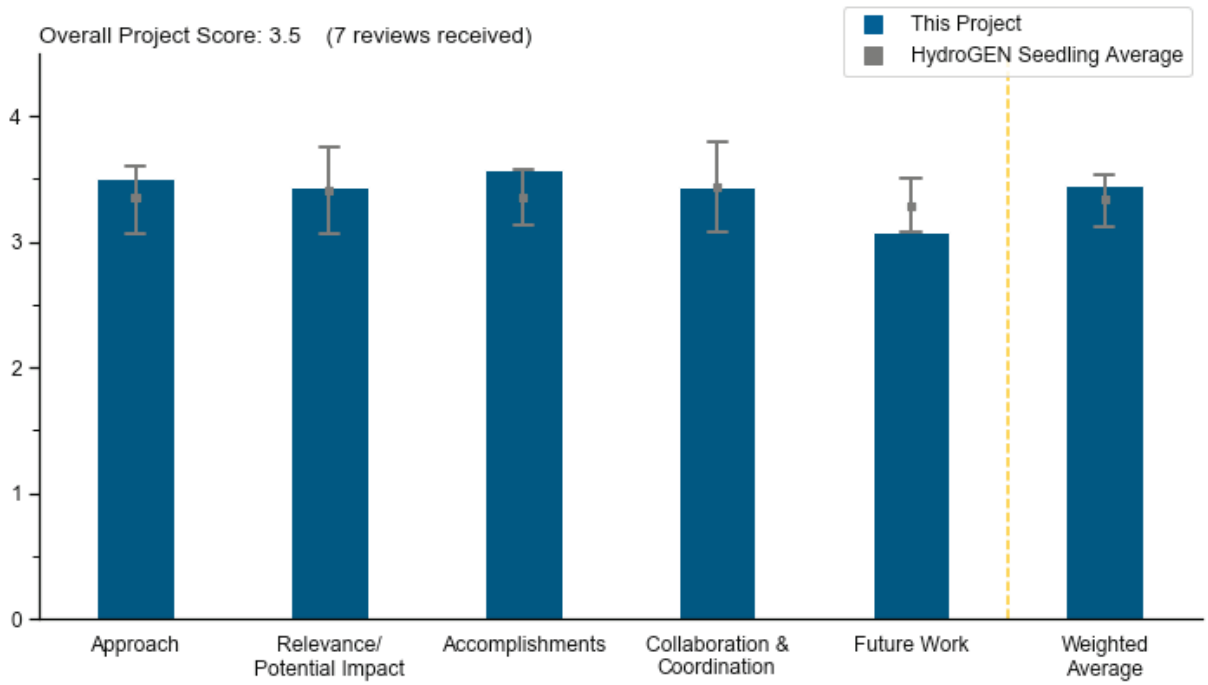
Project #P-165: Accelerated Discovery of Solar Thermochemical Hydrogen Production Materials via High-Throughput Computational and Experimental Methods

Ryan O'Hayre, Colorado School of Mines

Brief Summary of Project

The current state-of-the-art solar thermochemical hydrogen (STCH) material efficiency is approximately 2%, but development of an optimal STCH material could increase the efficiency beyond 60%. This project aims to integrate combinatorial synthesis methods with combinatorial theoretical calculations to rapidly discover new potential materials for use in two-step metal oxide cycles for STCH. The effort builds on prior collaboration between the project partners, which resulted in the discovery of two novel perovskite-based STCH candidates, and leverages the Energy Materials Network (EMN) model of merging high-throughput computational and experimental techniques to accelerate new materials discovery.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.5** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- This is a really good project. The team has screened 750+ compounds. The entire periodic table has been considered, as has been done on other multi-university research initiatives in other offices. The admittance criteria for the various elements from the table that are to be considered in the campaign are appropriate. Screening the compositions using pulsed laser deposition and multiple targets to deposit gradients across a surface, thereby accessing a spectrum of compositions, is also a methodology that proved fruitful in other multi-university research initiative works in other offices. There is some risk that the thin-film nature of the compounds produced results in solid-state configurations that are not representative; however, the principal investigator (PI) was aware of this and, by bringing the samples to high enough temperatures, was able to argue successfully that this risk is at a minimum. Furthermore, such thin-film approaches for liquid metals

have proven fruitful in the past. Those systems are even more difficult to work with because oxidation must be prevented. In perovskites, there is no such oxidation concern. The optical method of screening for activity using color and color changes is beautiful. The researchers have done top-notch work there, including using off-the-shelf commercial-quality scanners and building five color references into the sample arrays against which to baseline the technique. The choice of analytical technique represents a clear understanding that the activity is obtained from transition metals with electron occupancy in their valiance shells. This is classical inorganic chemistry and materials science at its finest. There is some focus on "super-structures" or "super-patterns" in how the crystals fill space. The project team should be aware that two-dimensional phenomena sometimes do not succeed in filling three-dimensional space.

- The approach in this project is a great complement of theory, synthesis, and characterization and builds off the PIs' previous collaborative success. Targeting lower acceptable maximum temperatures (T-max) is excellent and needed to enable the STCH technology. The project makes use of a well-thought-out methodology in computations of materials properties, which is a really nice component of the project. While the combinatorial pulsed laser deposition (PLD) that enables screening is useful, it may not produce thermodynamic materials, e.g., there is a lack of crystallization.
- The modeling, synthesis, and screening steps used in this project represent a powerful yet nascent approach to exploring and screening candidate STCH materials. Future opportunities to improve the physical tools employed are likely to improve the overall effectiveness.
- The project aims to "integrate combinatorial synthesis methods with combinatorial theoretical calculations to rapidly discover new potential materials for use in two-step metal oxide cycles for STCH." The key barriers are identified as the computational intensity of defect calculations, whether optical evaluation is sufficient (or meaningful), and how thin-film properties may differ from bulk materials. There is significant progress compared to the presentation given at last year's Hydrogen and Fuel Cells Program (the Program) Annual Merit Review (AMR), and there seems to be much greater synergy between the activities undertaken at the various locations. A shortfall in terms of the slide pack is that there is insufficient detail about the project plan to judge progress, resulting in confusion as to what is meant by budget period, year, quarter, or milestones without a Gantt chart or something similar. This makes it somewhat difficult to review progress performance against the scope of work for budget period 1.
- The team has a very good focus on targets and protocol development. The value of STCH from a Program perspective is questionable, however. Perhaps this catalyst screening protocol can be useful for other catalyst development work.
- The project efficiently combines high-throughput synthesis with appropriate modeling to further accelerate the identification of possible redox materials that are able to lower the temperature as necessary to close the thermochemical cycle. The evaluation is based on thin films, which might be different from bulkier materials that are necessary for large-scale hydrogen production, as the material is a reaction partner and not a catalyst. The optical analysis methods are fast and therefore appropriate for the idea of accelerating the process, but they may not be not sufficient for characterization. A similar simplification was chosen for the models, which might not be precise enough to fully predict the materials. However, speed was also in the focus here. The chosen methodology seems to be appropriate for identifying promising candidate materials.
- The Colorado School of Mines (CSM) team takes a combined, experimental, computational go-fast/go-slow approach to identifying new materials for solar thermochemical water splitting. The team also has clearly defined targets of achieving ~75 µmol H_2/g material, with a re-oxidation ratio of at least 10:1 H_2O:H_2, with reduction and oxidation temperatures of 1350°C and 850°C, respectively. While these are good targets, there is no clear identification of the materials properties needed (i.e., specific delta H, delta S) to achieve this goal, though the project does identify a wide range of delta H's (2.5–4 ev), which is far too wide. Computationally, the researchers are relying on rapid density-functional-theory-based screening to assess perovskite structure candidates for high activity. Through a down-select method, they have identified key cation components that are "good" for STCH. These are then combined into new structures for detailed analysis, including defect-formation energy calculation. This approach seems fruitful and has resulted in the identification of several interesting new structures. Experimentally, the project takes a colorimetric approach to rapid screening, where combinatorial PLD provides an ability to rapidly produce many compositions simultaneously. Colorimetric results, while an interesting technique, show only redox activity at the desired temperatures; to be significantly useful in assessing materials, thermodynamics are needed to see whether the materials meet the desired reduction thermodynamic characteristics. The "slow"

experimental piece takes an appropriate approach and has delivered interesting results, particularly the ability to form both layered and simple perovskites with substantially different properties. The team is clearly well integrated into HydroGEN, working with both nodes and other teams. The budget is a bit high for the amount of proposed work and the work portion that is being conducted at CSM as opposed to the nodes.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The project seeks a "goldilocks" material that balances stability, temperature reduction, production rate, and kinetics to achieve DOE targets. In the absence of engineering models, the performance of ceria is treated as the "gold standard," and project targets are defined based on a decrease of the peak (reduction) temperature to 1350°C and hydrogen production per gram of active material that must exceed that of ceria. This is well aligned with the Program's goals and objectives, and also supports the HydroGEN consortium mission. The project has strong potential to meet ultimate DOE targets, providing that project metrics are achieved. The most challenging aspect appears to be the steam-to-hydrogen ratio, as the performance of perovskite materials evaluated to date decreases rapidly at lower steam-to-hydrogen ratios.
- This project is highly relevant to Fuel Cell Technologies Office (FCTO) goals. While a clear path to $2/kg of hydrogen is not shown, this is not needed at this stage of research and development. New materials efforts with lower T-max are needed to enable STCH.
- This program advances the DOE goals of STCH materials identification. The experimental work is interesting, particularly the ability to form different structures of perovskites and the use of combinatorial experimental approaches. The computational work seems to have significant overlap with the approaches of other members in the HydroGEN consortium, especially since the computational work has been confined to perovskite structures. It is worth assessing whether it is worth having three projects with such similar computational approaches. While ideas are being leveraged between the projects, there appears to be significant overlap and repetition of work.
- At these early stages of STCH technology development, the fundamental materials focus of this project is extremely important.
- This is good work on catalyst development, notwithstanding the applications to STCH.
- The project aims to accelerate the search of candidate materials and does this very efficiently. However, because of the simplification, it is possible that effects may be missed or underestimated. However, the work will lead to candidate materials and therefore contribute to the goal of $2/kg hydrogen. As with all materials-focused projects, the efficiency of the material is only one aspect in achieving this goal. Without developing technologies, a market introduction will not be possible, and the goal will stay theoretical.
- This is a "get it done" kind of project. Even with all of the best modeling, one still needs to synthesize and characterize the "hits" from the modeling effort. This project can do that at the scale the modeling needs, thereby providing answers about the perovskite class's capabilities. Perovskites continue to hold relevance for the Program; however, the variation in materials properties seems to be occurring in a band or "smear" of values that is just not quite "outstanding." Therefore, a disruptive discovery must occur, or engineering and system design must shoulder any burden of the materials' performance shortcomings, if there are any. Perhaps the layered perovskites reported in this project are one such approach to enhancing the materials properties, but that has yet to be proven. The PI suggests that simple perovskites may be assembled into a layered structure, and that this structure can change the thermodynamics. It is not yet clear that it can do so enough to be disruptive.

Question 3: Accomplishments and progress

This project was rated **3.6** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- This project represents the "gold standard" in using high-throughput experimental methods to validate, verify, and potentially exploit materials science and related discoveries. It is difficult to imagine better accomplishments or progress; perhaps an improvement would be better integration with the other perovskite works in the portfolio.
- Setting up this multifaceted process is impressive progress. The CSM team is due congratulations for discovering a new layered perovskite.
- The project is on a good path. It continuously improves the rapid screening thin-film technology. It could identify interesting candidate materials that fit the milestones. However, to make substantial statements on their applicability for large-scale hydrogen production, the materials need to be proven in a relevant environment.
- A new STCH compound has been discovered, as guided by simulations, and at least one more new compound was identified. This is excellent. There were questions as to the value of the combinatorial approach, and it would be good to show that this can produce relevant films. The combinatorial method of estimating oxygen content from color is highly qualitative, and the value of this was not demonstrated.
- Significant progress has been made in identifying new materials, particularly in terms of Ce-containing compounds, and in the experimental validation and characterization of the materials. These achievements are made through a combination of work from the DOE nodes and the work at CSM. While the researchers have met one of the go/no-go milestones, namely exploration of five families of materials, they have not met one of the other go/no-go milestones: the production of hydrogen in water-splitting tests at Sandia National Laboratories and CSM.
- The metrics, deliverables, or timing on which the project is to be judged are not clear. However, what is clear is that the project has advanced significantly since the last AMR and is demonstrating good progress toward the DOE goals and the HydroGEN mission. It is good to see that the project now has a maximum steam-to-hydrogen ratio of 10:1, as this is important for enabling the necessary solar-to-chemical conversion efficiencies. The presentation includes data from all partners in a holistic way that suggests the project is moving forward at all levels, although there are still some unresolved questions about the validity and usefulness of the thin-film combinatorial approach.
- The project is accomplishing and meeting milestones, but the project needs to focus on achieving the truly mild reaction conditions. The team could possibly look at Ellen Stechel's presentation from Arizona State University (P-168) for direction on first principle development.

Question 4: Collaboration effectiveness

This project was rated **3.4** for its collaboration and coordination with HydroGEN and other research entities.

- The collaboration appears to be excellent. The team has established the right connections to efficiently integrate the competencies of other HydroGEN partners into the project. This improves the work in all areas, especially in the production of thin films and the analytic description of the identified candidate materials, but also in the efficient modeling of the substances. However, further improved analytics would add value to this.
- There is excellent collaboration with HydroGEN partners, including with the National Renewable Energy Laboratory for simulations and combinatorial synthesis and Sandia National Laboratories for testing. There are really good interactions within the EMN.
- The CSM team has shown itself to be very effective in working with HydroGEN, the nodes, and other members of the STCH materials community. These continued resources are critical to the project's success. There appears to be little-to-no engagement in benchmarking or data-sharing activities such as the Data Hub.
- This was one area that appeared less than fully effective at the previous AMR. It is pleasing to see that the project is now well linked at various partner institutes and that this engagement with the EMN is proving to be extremely valuable in moving the project forward.

- Slide 23 does well in defining which collaborator has contributed to which task, lending a sense of ownership and accountability. The effectiveness of the collaboration is very high.
- The collaboration and coordination with the other partners appears to be very good, judging from the results. However, the presentation did not discuss this point.
- There is good collaboration with EMN and the national laboratories.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The next year of the project is priced commensurate to the first year. The project is pursuing the innovation discovered in year 1 by looking for layered materials and more complex perovskites. The performance targets for these materials in the targeted application (i.e., water splitting) are well defined.
- The proposed work is presented only at a high level, but it seems appropriate and suitably targeted to enable end-of-project goals to be attained. The next go/no-go milestone is rightly seen as a challenging one.
- These plans are well thought out, with aggressive goals.
- The full characterization and advanced study of excellent candidate materials is the right way to go ahead. This is an excellent perspective. However, the proposed Hydrogen Analysis (H2A) hydrogen production models used for technoeconomic evaluation seem not to be appropriate, based only on materials development. The project does not generate any data besides the material that would justify developing the necessary input for the H2A. The team should consider what kind of solar system is appropriate for what kind of reactor, and if existing technologies or models are chosen, how relevant they are for the newly found substances.
- The future work is pointed in the correct direction, but it lacks specificity or a concrete plan. A more detailed plan of how to achieve the goals is needed. Additionally, more specifics are required to help hone the search; for example, it would be helpful to know what the characteristics are of the materials that are necessary to activate the 10:1 ratios.
- The proposed future work is appropriate. Where this project leads and what happens after year 3 was not discussed but is very important.
- It seems the future direction is just a continuation of the current work with the hope that a game-changing material will emerge.

Project strengths:

- This is a really great combination of theory, synthesis, and experiment targeting lower T-max to enable the STCH technology. The goals are highly relevant to FCTO, as new materials with lower T-max are badly needed. There is excellent collaboration with HydroGEN partners.
- This is a great project with a great PI. The experimental methods seem beyond reproach. The campaign seems well planned, and the analysis of results seems very careful.
- This project has leveraged machine learning and experimentation. The key strength of the project is the identification of cations that boost perovskite performance and focus on these materials. Additionally, the ability to make stable materials with similar compositions but layered or simple structures is interesting and potentially important. The multi-natured approach of materials production and analysis, particularly X-ray and thermogravimetric analysis, is good.
- The project's strength is clearly in the combination of fast, combinatory synthesis techniques with fast computing. In this way, it is possible to achieve results efficiently. They might not be the most precise results, but they show a direction in which further development will be promising.
- The project is well scoped and seems to be effectively leveraging the expertise within the EMN.
- The project is doing good technical work; many materials have been screened.
- The project's approach, accomplishments, and team are key strengths.

Project weaknesses:

- As the more complex layered structures and higher-order perovskites begin to be pursued, it will be interesting to see how the team manages the role of the processing parameters in synthesis and preparation. It remains to be seen whether the project will continue to be sophisticated, employing a design of experiments or some such similar and recognized approach for process development, or if the project will adopt an Edisonian trial-and-error approach.
- The importance and abilities of the optical analysis for assessing the detailed thermodynamics of the materials seem to be low; therefore, it is questionable if this is adding to the project or just taking up resources. More detailed plans for year 2 are needed. It seems as if a significant portion of work is being conducted at the laboratories; it will be useful to have a clearer delineation of what is being done at CSM and what the CSM team's contribution is. Importantly, there is significant scope overlap between STCH projects, leading to significant duplication of effort.
- The methodology is focused mainly on acceleration, but it lacks precision. This could result in overlooking some principles that might be important for further development. The work is not sufficient for a technoeconomic analysis (TEA) in H2A. This is the case for all materials-focused projects under HydroGEN. Therefore, the project would be more efficient if the work were concentrated on specific materials developments.
- Some of the concerns raised at the last AMR about the usefulness of the thin-film testing remain unresolved in terms of the validity of the optical assessment. While it is apparent that color is a useful indicator that something is happening, it is less clear what that might be or what exactly the material is.
- The combinatorial method of estimating oxygen content from color has shown limited value and should be critically assessed. The combinatorial PLD enables screening; it may not produce thermodynamic materials.
- Further consideration is needed for hardware enhancements and the longer-term path going forward.
- It is not clear what the proposed value is.

Recommendations for additions/deletions to project scope:

- It would be valuable to have some harmonization of target performance across the HydroGEN projects. Each project has somewhat arbitrarily identified targets, which could benefit from some inter-comparison to ensure that each set is sufficient to meet or approach DOE targets. All of the HydroGEN project presentations should be made clearer in terms of the project plan, performance, and expected timeline.
- The project team should consider incorporating a metamaterial-like pattern in the layered structure, thereby focusing internal lattice potentials to specific layers and encouraging "oxygen hop" through an averaged background potential that is elevated but, by being constrained, not destructive.
- Based on the results from year 1, it seems that the optical analysis is of limited value and should be cut. Additionally, TEA and deep thermodynamic characterization are desirable in the second project period for some materials, rather than leaving this work until the third.
- The project could be improved by additional analytical tasks that would help to better describe the materials. The project would also be strengthened if it could focus on its materials-related work and not on the H2A. Such an analysis that is based only on materials seems inappropriate.
- The combinatorial method of estimating oxygen content from color should be critically assessed, and the clear value should be demonstrated.
- It is recommended that the team really focus on evaluating needs and determining how to screen materials that meet these needs.

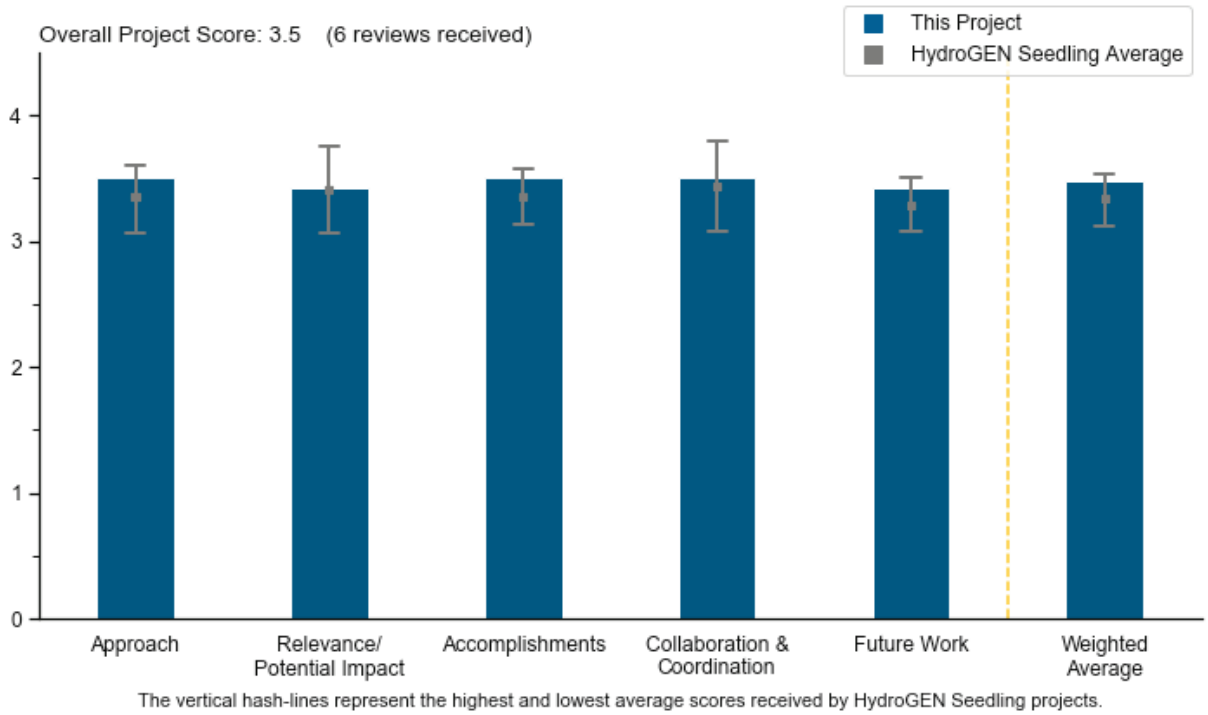
Project #P-166: Computationally Accelerated Discovery and Experimental Demonstration of High-Performance Materials for Advanced Solar Thermochemical Hydrogen Production

Charles Musgrave, University of Colorado Boulder

Brief Summary of Project

The project objective is to utilize machine-learned models coupled with ab initio thermodynamic and kinetic screening calculations to accelerate the research, development, and demonstration (RD&D) of new solar thermochemical hydrogen (STCH) materials. The approach will rapidly screen a vast number of new candidate metal oxide materials for stability, thermodynamic viability, and kinetics. The project will utilize experimental techniques to evaluate thermodynamic and kinetic properties of new materials to provide feedback to the computational thermodynamic and kinetic screening effort.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.5** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The approach of the project to perform the work is excellent. It is innovative to combine machine learning (ML) with *ab initio* simulations to reduce calculation effort while increasing the number of screened substances. However, even ab initio calculations are an approximation of reality. The calculation of each structure is very time-consuming compared to other calculation methods that have a higher grade of simplification but lead to the same hints as to which direction of the search for the best materials. Still, it gives additional insight into the structures; therefore, the higher computational effort is also of high value for understanding the systems.
- This project is the "gold standard" in terms of how high-throughput, computationally aided materials discovery and "proving out" how to proceed. This is outstanding.

- The project has a very solid approach of predictive modeling followed by first principles screening and experimental parametric testing.
- The project aims to "develop and utilize machine-learned models coupled with *ab initio* thermodynamic and kinetic screening calculations to accelerate the RD&D of new STCH materials." This is complemented by experimental validation in thermogravimetric analysis (TGA) and the stagnation flow reactor (SFR) at Sandia National Laboratories (SNL). The main barriers identified are the huge possible compositional space for materials and the vast number of candidates. There seems to be good progress, although some slides are identical to the presentation given at last year's Hydrogen and Fuel Cells Program (the Program) Annual Merit Review (AMR). There is good synergy between the activities undertaken at the various locations. A shortfall in terms of the slide pack is that there is insufficient detail about the project plan to judge the progress, resulting in confusion as to what is meant by budget period, year, quarter, or milestones without a Gantt chart or similar. This makes it somewhat difficult to review progress performance against the scope of work in budget period 1.
- This project seeks to use computation to guide the development of new STCH materials. The use of ML in this space seems novel, but as with all materials applications of ML, the datasets can be very small. The focus on surface versus bulk kinetics is novel and an important part of new STCH materials. The temperature reduction goals seem to be modest. There is a strong need to vet the computations with experiments as a next step.
- The approach to performing the work is technically sound, but the project needs to do more work around the value of STCH, even if amazing catalysts are found.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- This project is brilliant. Consequently, it begs the question of whether this is it for perovskites. Perovskites continue to hold promise in delivering on DOE targets. However, at some point, either a breakthrough combination of elements will be discovered, or the potential of these materials to satisfy the performance requirements exists in a band and that "smear" of capability does not vary as widely as hoped. The materials properties that are available then must be exploited by some process and/or engineering design that makes up for performance gaps.
- The innovation in this project is to use ML models to predict perovskite stability and thermodynamic properties to reduce the solution space for a workable STCH material. In the absence of engineering models, the performance of ceria is treated as the "gold standard." Project targets are defined based on a small decrease in the peak (reduction) temperature to <=1450°C, and hydrogen production per gram of active material must exceed that of ceria (200 vs. 130 µmol/g). This is aligned with Program goals and objectives and also supports the HydroGEN consortium mission. The project has good potential to meet the ultimate DOE targets, providing that project metrics are achieved. The most challenging aspect for successful implementation appears to be the high steam-to-hydrogen ratio, although it is noted that "oxidation will either be operated at H_2O:H_2 ratios of less than 1000:1 or a [techno-economic analysis (TEA)] will be conducted to verify that higher H_2O:H_2 ratios are economically practical with the new material."
- At this early state of STCH technology development, the materials research being carried out by this project team is essential to achieving the Program goal of <$2/kg of hydrogen.
- While a clear path to $2/kg is not shown, this is not needed at this stage. New materials with higher hydrogen production rates are needed to enable STCH. The reduction in maximum temperature is very modest.
- The highly computation-based results give interesting insights into the systems and are an important contribution to HydroGEN. However, the applied methodology is far away from any application of the described materials, and therefore the impact on the $2/kg hydrogen goal is very indirect.
- The development of these catalysts may provide broadly applicable methodology. STCH is not particularly relevant to the development of the hydrogen economy.

Question 3: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- This project should serve as a benchmark of excellence for this kind of work. The team also did a great job on the publications.
- The project is progressing very well. The ML showed very good results, and the calculated systems are promising. The parameter of stability opens up the possibility to synthesis efficiently, promising candidate materials with a very high probability of success. Overall, this innovative attempt seems to be heading in the right direction. Some more proven materials will underline its potential.
- The new descriptor (replacing the Goldschmidt tolerance factor) for perovskite stability is a significant advance and helps reduce the number of calculations.
- The project has had very impressive accomplishments on a complex, multifaceted effort.
- It is not clear on what metrics, deliverables, or timing the HydroGEN projects should be judged. However, what is clear is that the project has advanced since the last AMR and is demonstrating good progress toward meeting the DOE goals and the HydroGEN mission. The various activities are all moving forward, although some accomplishments have been previously reported. The results indicate an improved understanding of some of the underlying drivers of performance, although it is focused more on theory rather than practical demonstration. Conspicuous by its absence is the TEA work that was flagged for the National Renewable Energy Laboratory (NREL); this is mentioned, but no results are reported. Some high-level analysis of necessary performance targets would be valuable.
- This project needs experimental validation to meet the go/no-go decision points.

Question 4: Collaboration effectiveness

This project was rated **3.5** for its collaboration and coordination with HydroGEN and other research entities.

- There is excellent collaboration with some HydroGEN EMN partners, especially NREL for simulations. There appear to be good collaborations with SNL in Livermore, California, and Albuquerque, New Mexico, for STCH testing and materials characterization, respectively.
- The collaboration seems to be appropriate for the structure of the project. The right competencies from HydroGEN are added to the capacity of the project team. The input from the collaborators is necessary and useful. The collaboration is not too broad, so it can efficiently support the project team in achieving its project goals.
- After listening to several of the STCH catalyst presentations, it is clear that there is a strong community and collaboration around this topic. This project, like the others, has strong formal and informal collaboration.
- There is no doubt that the excellent performance of this project may be attributed, in part, to excellent collaborations.
- The project's outstanding collaboration and coordination is evidenced by the impressive results.
- The project reports some nice results from the various project partners, although the tasks do seem a little disconnected in some sense, rather than truly integrated into a cohesive whole. For instance, it is not clear what the status is of Task 4, the SFR work at SNL.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The proposed future work is exactly what is required to arrive at a firm, defensible conclusion about the potential of perovskites as a materials class. It is a logical extension of the current phase.
- The proposed future work is exactly what is needed to achieve the goals successfully. It concentrates on the key questions of the project and will use the resources efficiently to achieve the goals.
- The future plans are strong, with aggressive targets, but lack a strong connection to experiments.

- The development of first-principle needs makes more sense than screening millions of compounds, but when coupled with Ellen Stechel's work at Arizona State University, the future work for this project looks good.
- Slide 15 suggests that a considerable amount of work is necessary to meet the next go/no-go milestone. This will be dependent on the experimental work being done at SNL, which has either not been started or was not reported at the AMR.
- It is unclear where this project leads, what work should follow this project, or what the pathway forward is.

Project strengths:

- This is an outstanding principal investigator (PI), able to clearly articulate complex campaigns of discovery in easily relatable ways. There is a simple, sound, logical progression of plan and effort. The conclusions are succinct and convincing. On slide 6, the PI did well to articulate the root cause of the systematic error in the correlation plot between the sure independence screening and sparsifying operator (SISSO) and quasi-harmonic models. The magnitude of this systematic error was the same when compared to experiment. The project does well to include various statistical measures of dataset fits to lines and other things. The technical effort is beyond reproach.
- This project takes a novel approach to materials design, incorporating ML and kinetics; it has been highly productive, with some impactful publications.
- The combination of ML and ab initio calculations is innovative and helps with reducing computational effort without losing the depth of the calculations.
- The project is strong theoretically; it seems to be making some good progress at understanding some of the drivers of STCH performance and finding effective ways of predicting properties.
- The project has done good technical work and has a strong record of collaboration and publication.
- The project's approach, accomplishments, and team are all impressive strengths.

Project weaknesses:

- The project as reported seems a little disconnected from the experimental stages, which will be critical for continued progress. This may be intentional on the part of the project lead, but compressing all of the experimental work may prove challenging.
- The final deliverable is purported to be less than 10% loss in hydrogen production capacity between 100 and 200 cycles. While this is certainly an early-technology-readiness-level project, it should have identified the absolute best candidates from the entire class of perovskites. Thus, with 10% capacity loss after only 200 cycles, the material is not adequate, and either a new material needs to be chosen (which should have been chosen in the first place), or a process or engineering design needs to be devised to "save" the material from such a fate. The PI did recognize regeneration as a possibility, although he did admit it is a complex technoeconomic consideration.
- Validation is not the major topic of the project. A closer link to validating efforts would strengthen the project.
- The coupling of the computations to the experiments was not convincingly demonstrated. It was unclear what new materials were actually synthesized and tested. The temperature reduction goals are modest.
- The commercial context, path forward, and ideas for improved hardware and software are unclear.
- The value of STCH is questionable.

Recommendations for additions/deletions to project scope:

- The project is on the right track. The work should be carried out as proposed. A closer link to practical work that could validate the results more thoroughly would strengthen the project.
- It would be valuable to have some harmonization of target performance across the HydroGEN projects. Each project has somewhat arbitrarily identified targets, which could benefit from some inter-comparison to ensure that each set is sufficient to meet or approach DOE targets. It was encouraging to see that this project has a TEA component, but it was disappointing that it has not been made a priority or a necessary component at this stage. All of the HydroGEN project presentations should be made clearer in terms of the project plan, performance, and expected timeline.

- The identification of knowledge and technology gaps should be considered, as should the next steps following the end of this project.
- In future work, it is recommended that the team connect the computational characterization of the material catalytic activity with the first-principle elucidation of catalyst needs.
- The team should develop a stronger coupling with the synthesis teams in HydroGEN.

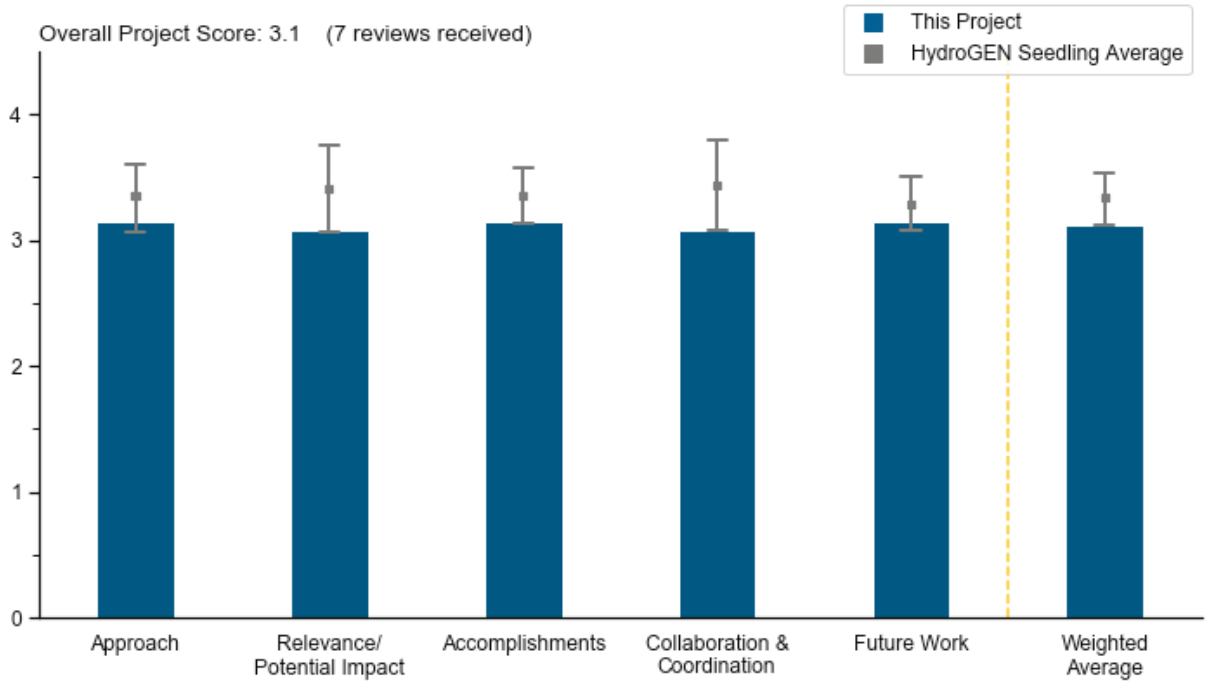
Project #P-167: Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

Chris Wolverton, Northwestern University

Brief Summary of Project

The project objective is to utilize a computational–experimental approach, combined with materials design strategies to quickly discover and demonstrate novel thermochemical materials with properties superior to the state of the art. The project will investigate what is an enormous compositional space of materials utilizing high-throughput computational and experimental methods to identify promising compounds that show (1) ground state stability/ synthesizability, (2) thermodynamics favorable for <1400°C reduction, and (3) thermodynamics favorable for facile water splitting.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.1** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The approach in this project is a combination of theory and synthesis to target stable and effective materials for solar thermochemical hydrogen (STCH) production; it builds off some previous collaborative success. There is a focus on perovskite-type oxides and a strong link between the simulations, synthesis, and characterization.
- The design map for acceptable materials is a good place to start. Understanding that validating computation using experimentation on simple materials is also a good approach.
- This is a pretty good project. It uses some straightforward, nuts-and-bolts approaches to screening perovskite materials.
- The three-step statement of work is simple and logical, yet extremely challenging.
- The project has a clear strategy to use fast, in silico screening methods built on sound experimental data of model substances. Therefore, the models used are very close to real data and promise to generate high-

quality results that will lead to a fast and efficient identification of promising candidate systems for STCH production. However, the work is still very far away from real applications, and the necessary conditions for use in the field are not taken into account.

- The project aims "to combine high-throughput computational and experimental exploration of oxygen off-stoichiometric oxides and phase change materials for enhancing the efficiency of [solar thermochemical] production of solar fuels." The project as presented is quite loosely formulated, and the barriers are not really articulated. This lack of an articulated focus is compounded by the nature of the slide pack, which has insufficient detail about the project plan to really judge progress. This results in confusion as to what is meant by budget period, year, quarter, or milestone without a Gantt chart or something similar. Also confusing is that the start date of the project has moved forward 18 months from October 1, 2017 (as reported in the 2018 Hydrogen and Fuel Cells Program [the Program] Annual Merit Review [AMR]) to April 1, 2019, in this year's AMR. Thankfully, the year 1 scope of work is well explained, and the experimental work is well described.
- The outlined approach was to use a combination of known computational (density functional theory [DFT] brute force) and new and known experimental (thermogravimetric analysis [TGA] and electrochemical impedance) methods to identify new materials for STCH production. Computationally, the approach is slow, though able to succeed given sufficient time and resources and, of course, the existence of materials with the desired properties. The experimental approaches and innovations are the use of continuous TGA runs, as opposed to stepped runs, to evaluate non-stoichiometry–temperature–pressure relationships. This looks to enable the far faster and more reliable extraction of materials thermodynamics. However, it has a severe drawback in the need to stay within a single perovskite sub-structure; changes in structure between, for example, hexagonal and cubic seem to be a problem for this method, despite occurring at conditions that are critical for STCH materials. No mention or description of electrochemical analysis is made, so its appropriateness, etc., cannot be evaluated. There appears to be almost no integration with HydroGEN. Interactions seem to be present only to check a box rather than as a useful tool.

Question 2: Relevance/potential impact

This project was rated **3.1** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The objective of this project is to "identify compounds which show: (a) synthesizability, (b) thermodynamics favorable for <1400°C reduction, and (c) thermodynamics favorable for facile water splitting. State-of-the-art currently CeO_2 and Sr- and Mn-doped LaAlO (SLMA) perovskite." The innovation in this project is to compare thermodynamic properties for simple perovskite materials from experimental investigations against predictions from computation. While the performance targets are less explicitly stated than in the other HydroGEN projects (e.g., there is no target production rate), the goals are well aligned with DOE targets and the HydroGEN mission.
- This fundamental materials work is essential to achieving the goal of $2/kg hydrogen.
- As with several of these STCH papers, the work is technically good and could be broadly applied to catalyst or materials development. However, the work around STCH should be evaluated from a Program standpoint.
- The work seems to be very much oriented around basic research. The connection to an application of the results in real hydrogen production plants seems to be very weak. Therefore, the impact in achieving the $2/kg hydrogen goal is low. However, the work is scientifically excellent and might lead to very important results.
- New stable materials with higher hydrogen production rates are needed to enable STCH. A path to $2/kg is not shown, but it is not needed at this stage. The targeted maximum temperature (T-max) is rather high.
- Perovskite materials continue to hold promise to achieve the DOE's cost targets. However, with the new high-throughput computational screening methods (of such high fidelity to experiment), it may well be that the materials discovery stage is either (a) coming to a close or (b) in need of (or currently evolving into) a more complex, super-structure discovery process (the so-called layered perovskites discussed in other projects). Ultimately, it may need to be considered whether the process and the engineering can deliver where the materials may not.

- The project is aimed in the correct direction; however, some self-imposed limitations on experimentation, such as phase-change restrictions, likely hamper the likelihood of success in analyzing STCH active materials. The method of computation seems slow, therefore increasing the challenge of finding the desired materials; this is particularly apparent when compared to the progress made by other projects. The computational work seems to have significant overlap with the approaches of other HydroGEN members, especially since the computational work has been confined to perovskite structures. It is worth assessing whether it is worth having three projects with such similar computational approaches. While ideas are being leveraged between some of the projects, there appears to be significant overlap and repetition of work. This project has not leveraged HydroGEN resources, nor does it seem to integrate well within it.

Question 3: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project presents excellent results by coupling measurements with DFT simulations. A very high number of potential candidate materials could be screened. This is an important input for the DOE goal of identifying the most promising systems for STCH. However, it is very far away from application. Therefore, the main $2/kg hydrogen goal cannot so much be the focus as the actual behavior of the materials. This should be seen as a strength, as the materials alone will never be the key factor of the actual cost of hydrogen. However, their efficiency will be important to designing the right plants.
- The project has been highly productive, with significant progress made in thermodynamic measurements, computation and open databases, and synthesis.
- The team is making good progress toward project goals early on in the project. The validation of 12 perovskites with experimentation is very important for guiding future work.
- For the amount of time that has elapsed, and for the relatively small dollar amount spent, this project has made great progress.
- As noted in other projects, it is not clear how the HydroGEN projects should be judged in terms of metrics, deliverables, or timing. However, here, as elsewhere, there has been good progress in terms of results, and some nice techniques are shown for simultaneously evaluating ΔH and ΔS as a function of δ. Despite the reuse of some slides from the 2018 AMR, the new data presented shows encouraging progress. Missing from the presentation are results from the year 1 scope of work part (b): "validate high-throughput methodology for measuring thermodynamic property using thin film through electrochemical impedance."
- The team is due congratulations on the seven new predictions for stable double-perovskites with favorable water-splitting thermodynamics. To date, the project has shown that calculated O-vacancy formation energies are in some agreement with experiment (r^2=0.6). Additionally, the project has calculated ~10,000 materials. However, given the vast space of materials available, blind searching would seem to require significantly higher rates of materials calculation. The year 1 project goals were vague, and go/no-go points were not stated; this makes evaluation of the go/no-go decision difficult. The stated scope of work outlined three tasks: experimental measurement of 12 materials, validation of the electrochemical impedance technique, and starting high-throughput screening. The experimental measurement of 12 materials was completed; however, many of the materials studied are already known and therefore do not demonstrate additional progress toward DOE goals. There was no presentation of data regarding electrochemical analysis of materials or proof that this work was done at all. The high-throughput screening was initiated.

Question 4: Collaboration effectiveness

This project was rated **3.1** for its collaboration and coordination with HydroGEN and other research entities.

- The discovery of the layered perovskite STCH compound, the 2018 and 2019 publication, and the invited presentations are evidence of outstanding collaboration and coordination.
- The project has no doubt been able to make such substantial progress in such a short amount of time as a result of its great collaborations.
- There is good collaboration with both national laboratories and universities. There seems to be a strong collaborative community in this part of the Energy Materials Network.

- There are collaborations in HydroGEN nodes: the National Renewable Energy Laboratory for synthesis, Sandia National Laboratories for characterization, and one other seedling (Colorado School of Mines).
- The presentation seems to be strongly focused on the principal investigator's work, and it is difficult to gauge the nature and effectiveness of the collaboration described in slides 19 and 20.
- The project presented its collaboration within HydroGEN. This is appropriate, but compared to other projects, the network seems to be on the smaller side. Maybe a closer integration with HydroGEN and with more partners would improve the position of the project in the framework.
- There seems to be limited interaction with HydroGEN and the nodes, aside from one token high-temperature X-ray diffraction analysis. There is no discussion of interactions with benchmarking or protocols, nor was there discussion of use of working groups or the HydroGEN Data Hub.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The future work plan is strong, with aggressive plans for both the computational and experimental aspects of the project.
- The proposed work is exactly what is needed to achieve the scientific goals of the project.
- This is good future work. The only consideration is that the design map approach and the computational approach have shown great progress. Focusing more narrowly on advancing this work, rather than taking on several new objectives, would be most valuable. From a programmatic standpoint, not much value is seen in STCH. However, that is no reflection on the good work of this project.
- The proposed future work is an obvious extension of the current phase.
- The amount of future work appears to be quite substantial for what is presumably about the halfway point of the project (this is hard to gauge in the absence of a Gantt chart or something similar). It is not clear what go/no-go criteria have been agreed to with DOE for the next review.
- The proposed future work is vague in terms of both goals and methods. It does propose using methods developed in year 1, particularly in the computational area. There is no outline to connect how these works will meet end-of-project goals. Based on the work completed in budget period 1 (BP1), the amount required for BP2 is far too high and should be scaled back significantly to be more in line with the work completed and the apparent time dedicated to the project.
- There is no mention of how the team plans to move its work into initial follow-on applications.

Project strengths:

- It seems like a great idea to use electrochemical impedance spectroscopy to increase the throughput of perovskite candidate characterization. It would be interesting to see whether the colorimetric methods used in other projects correlate well with the electrochemical impedance spectroscopy proposed here. Slide 8 describes and employs some solid physical chemistry. Slide 16 does well to include the Pearson correlation coefficient, which is actually pretty good (0.88). It is important to include this because the R^2 value is not so good (0.63). Slide 17 has a really nice plot to show how most of the periodic table is being considered.
- The project is an excellent blend of theoretical calculation and targeted experimentation. There seems to be good progress in terms of developing methodologies for effectively evaluating thermodynamic properties.
- The project has a closely coupled and strong combination of theory and synthesis for targeting stable and effective materials for STCH. There are very good collaborations with HydroGEN.
- The researchers have corrected their previous assumption that cubic structures can be used to represent perovskite structures, and they have shown that the use of continuous TGA can be useful.
- The strongest part is that the project is starting from the design map (i.e., identifying needs) with experimental validation.
- The strength is the solid experimental foundation of the excellent simulations that lead to a very high number of screened potential materials.
- The approach, results, team, and collaboration are all impressive strengths.

Project weaknesses:

- The project has several weaknesses. Experimentally, no data or proof of electrochemical analysis has been provided, which was a key project component. Similarly, much TGA work was restricted to known and uninteresting compounds. Within the TGA data scope, the restrictions required to conduct continuous scans eliminate significant numbers of materials, particularly those that are likely to be interesting, i.e., materials with slight phase changes. No comment is made about experimental findings in relation to project goals or targets. The DFT work should aim to further identify what "ideal" materials are so that there is a concrete metric during screening. Additionally, methods to either simplify and/or minimize the search space or vastly increase screening speed are needed to achieve the stated goals. There is a clear lack of integration with HydroGEN in terms of using nodes and Data Hub resources. Given the overlap with the other two projects in terms of computational and experiment work proposed and presented, it is worth assessing whether there should be three projects with such similar approaches. This project seems to overlap significantly but is not leveraging the knowledge or method development generated in the other projects.
- The project as reported seems to be more of a single-institution effort rather than an effective HydroGEN collaboration. The go/no-go metrics are not clearly articulated, so it is difficult to see whether the project is adequately defined in terms of material property requirements.
- The project is using TGA as a primary means of generating experimental data. There is nothing wrong with this, per se; however, it takes a long time and is somewhat incongruous with the high-throughput strategy.
- The project seems to be a little more decoupled from HydroGEN than the others in this area. A stronger link to application would help to improve the analysis of the results.
- The targeted T-max is rather high.
- There is a possibility of diluting the impact by doing too much in the future work.
- The lack of a pathway to commercial applications is an area of weakness.

Recommendations for additions/deletions to project scope:

- The project is very well structured. It does not need any additions or deletions. However, a better integration into the HydroGEN framework might improve the excellent work.
- The researchers should focus on accomplishments, but otherwise they are doing great work.
- It would be valuable to have some harmonization of target performance across the HydroGEN projects. Each project has its own targets, which could benefit from some inter-comparison to ensure that each set is sufficient to meet or approach DOE targets. All of the HydroGEN project presentations should be made clearer in terms of the project plan, performance, and expected timeline.
- The budget for the next performance period is not aligned with the work proposed, given the year 1 performance. In particular, the use of electrochemical analysis should be reassessed, as the project has not proven the ability to do this work.

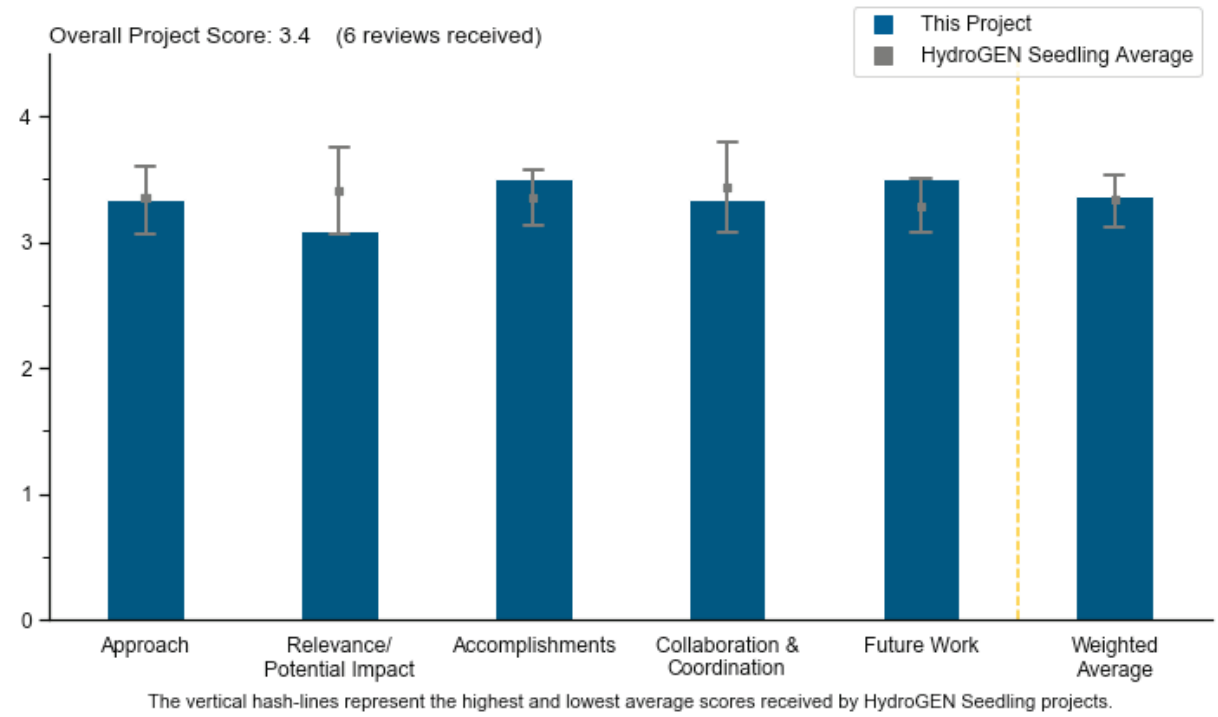
Project #P-168: Mixed Ionic Electronic Conducting Quaternary Perovskites: Materials by Design for Solar Thermochemical Hydrogen

Ellen Stechel, Arizona State University

Brief Summary of Project

The project objectives are (1) to contribute to improved solar thermochemical hydrogen (STCH) materials discovery by providing strategies to boost solar-to-hydrogen thermal efficiency and (2) to provide experimentalists with crucial input to synthesize, validate, and perform further testing on promising candidates. The project will apply first principles computational materials design capability to calculate and validate chemical potentials for complex off-stoichiometric redox-active mixed ionic electronic conducting perovskite metal oxides. The end goal is to determine design principles for optimal and discoverable materials that have the potential to perform better than ceria, meet the target efficiency (solar-to-hydrogen thermal efficiency >30%), and approach the ultimate production cost goal of <$2/kg H_2.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.3** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The project is strategically focused on thermodynamic principles of the materials used for thermochemical redox chemistry. This is a very promising way to identify promising candidate materials. The work is based on excellent theoretical knowledge, as well as practical experience with concentrated solar radiation. Therefore, it seems that the project is seriously taking into account the difficulties of transferring the results from the simulation into application.
- The project goals are well articulated: "to determine the optimum reduction enthalpy (ΔH) that balances degree of reduction, hydrogen yield, and temperature swing and, given that, strategies to tune the ΔH." Similarly, the barriers are well described, and the project approach is well constructed, with complementary tasks.

- The approach is a well-conceived, simply described, multifaceted body of work.
- This is a theory effort aimed at providing guidance for materials design by first principles calculation of defects at a very fundamental materials level. There was some text mentioning "inverse design," but this was not explained. The key goals are increasing reduction capacity (delta to 0.15) but at only modest temperature reduction, as well as improving uncertainty; these are valuable goals. The question of "how good is good enough" is very important, but the method to achieve this was unclear. It was also unclear how the experimental teams will use the results.
- The first principles approach was appreciated. However, the value of the STCH processes overall is questionable.
- For this project, it was a little bit hard to get the point.

Question 2: Relevance/potential impact

This project was rated **3.1** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The project has a good balance of theory and experimental work using modeling to reduce the number of candidate materials, as with the other HydroGEN projects. However, this particular project seems the most focused on application of the four oxide discovery projects, and it is perhaps the most robust in terms of considering what is required to achieve the DOE targets. The project arguably "enhances the broader HydroGEN by providing a missing link between computation, experiment, efficiency, and cost of H_2."
- The simulations are valuable to help guide new materials efforts needed for STCH; uncertainty quantification is important here.
- This work is essential to achieving much-needed STCH performance breakthroughs.
- Developing the thermodynamic first principles for materials development should be broadly applicable to DOE and other technical developments. The value of STCH is dubious, but that is a concern for the Hydrogen Fuel Cells Program (the Program).
- As in all other material-oriented projects, the step into application is very big. The results of the project will certainly be important. However, the impact on the $2/kg hydrogen goal will be limited.
- Perovskites continue to hold promise for the Program; however, this project did not do a good job making clear what values constitute success. The targeted reduction capacity values seem very high—five times the state of the art—but the accuracy of the model for the chemical potential is targeted to be +/-20%. If the reduction capacity values approach anything like the multiple the project is pursuing, then it is not clear that 20% would matter; the system would have increased performance by 500%. If the error budget allotted for this work is +/-20% error on a logarithmic scale (as seen on slide 11), then that is perhaps more commensurate with the reduction capacity being targeted, but then the error is just huge. On slide 9, the project claims to provide the missing link between computation, experiment, efficiency, and the cost of hydrogen; however, the cost of hydrogen may be generated only by high-fidelity engineering and technoeconomic models, of which there is little in this presentation.

Question 3: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- As noted in other projects, it is not clear how the HydroGEN projects should be judged in terms of metrics, deliverables, or timing. However, as elsewhere, it is clear that substantial progress has been made since the last Program Annual Merit Review. This presentation is nicely constructed to show that the project has a consistent and logical basis, and the data presented show promise in terms of material discovery, while at the same time recognizing just how tough the problem is in terms of the required performance.
- The project achieved excellent progress. As in all other related projects, the topic is extremely complex, and the work necessary to achieve the final goals will need more time. However, the team showed that the way ahead is very promising and will lead to important results.
- There is progress in achieving the goals, and there are predictions of ΔH for ceria and alloys. It seems that 20% accuracy is aggressive, especially over a range of temperatures and for high delta (reduction capacity)

where vacancies will start to interact. The work did not seem to account for the vacancy–vacancy interaction. It was unclear how close the team was to the go/no-go goal.
- For the dollars spent and the time elapsed, the progress is pretty good. There has been a publication and a few presentations. Perhaps two compounds have been identified as potential candidates.
- This is a good approach that involves defining the need, then finding candidate materials, rather than trying to characterize materials.
- The results to date bode well for future discoveries.

Question 4: Collaboration effectiveness

This project was rated **3.3** for its collaboration and coordination with HydroGEN and other research entities.

- The project is well coordinated and effectively leverages the appropriate expertise at institutions in the Energy Materials Network (EMN).
- The project is very well embedded in HydroGEN. It presents an excellent collaboration that is absolutely appropriate to achieve the goals.
- Publications from this diverse team are highly anticipated.
- The partnering with Princeton University Dean Emily Carter (outside of HydroGEN) is excellent, but it is unclear how much interaction there is with the synthesis groups. In principle, this can be strong, but this was not demonstrated. It was also unclear how the experimental teams will use the results.
- There seem to be many institutions identified as collaborators, and there is no doubt that some collaboration is ongoing. However, it seems like there might be too many collaborators or that the project is seeking to accomplish too much, and so each contribution is "diluted."
- It is unclear to what extent the team is collaborating with national laboratories on model development. However, this work may be outside the experience of the national laboratories. The collaboration with laboratories on synthesis is good, although it would be good to quickly transfer that work to a commercial materials partner who might accelerate the technology adoption.

Question 5: Proposed future work

This project was rated **3.5** for effective and logical planning.

- The project presented an excellent strategy to continue its successful work. The proposed actions are perfect to achieve the goals within the project.
- It is a good approach to develop models now that candidate materials have been identified.
- The project appears well managed, with a good understanding of where it is and what the next steps need to be.
- The team appears to have a clear vision of its path forward.
- This was brief but directed along the necessary lines.
- The work on (A,A')(B,B')O3 "quinary" perovskites seems interesting, especially if it can consider, respect, or reflect the so-called layered structure that others have observed. The quantification of the thermodynamic and/or kinetic benefits of these higher-order opportunities needs to occur. However, it is not clear that the layer structures or other natural phenomena are of large enough magnitude to be a game changer for perovskites. There is some mention of enhancing and/or refining some of the collaboration. Perhaps this will serve to focus the team's contributions.

Project strengths:

- This is a fundamental materials design project that targets new, badly needed materials for STCH. The key goals of accuracy and increasing capacity are excellent.
- The thermodynamic-based simulation is the clear strength of the project, along with the experience the scientists involved have with the application of the materials under real solar conditions.
- The project team has a successful history of working in perovskite materials and a strong working relationship with Sandia National Laboratories (SNL).
- This is an impressive piece of work that effectively utilizes the multi-institution competencies within EMN.
- The strength of this work is first principle development and comparison with experimentation.
- The project's goals, approach, team, collaboration, and results are all impressive.

Project weaknesses:

- A closer connection to application would improve this project. However, as the materials are the main focus, at least a little more effort on experiments might underline the successful modeling work.
- "Materials by design" is an aspirational goal that many fields have failed to achieve. This approach seems to come with considerable risk, with the uncertainty that propagates through the models and the currently vague nature of the engineered systems required to exploit the as-of-yet unidentified materials.
- The June 30 go/no-go milestone is quite close, and it is difficult to judge how the SNL work is tracking to deliver on this.
- There is no focus on reducing maximum temperature, an important issue in STCH. There seem to be limited interactions with experimental teams, especially in terms of synthesis.
- The value of STCH overall is questionable.

Recommendations for additions/deletions to project scope:

- The project works well. It should be continued as presented.
- The scope is good.
- It would be valuable to have some harmonization of target performance across the HydroGEN projects. Each project has its own targets, which could benefit from some inter-comparison to ensure that each set is sufficient to meet or approach DOE targets. All of the HydroGEN project presentations should be made clearer in terms of project plan, performance, and expected timeline.
- The team should improve interactions with the synthesis efforts in HydroGEN.
- Publication topic plans would provide context and direction at this point.

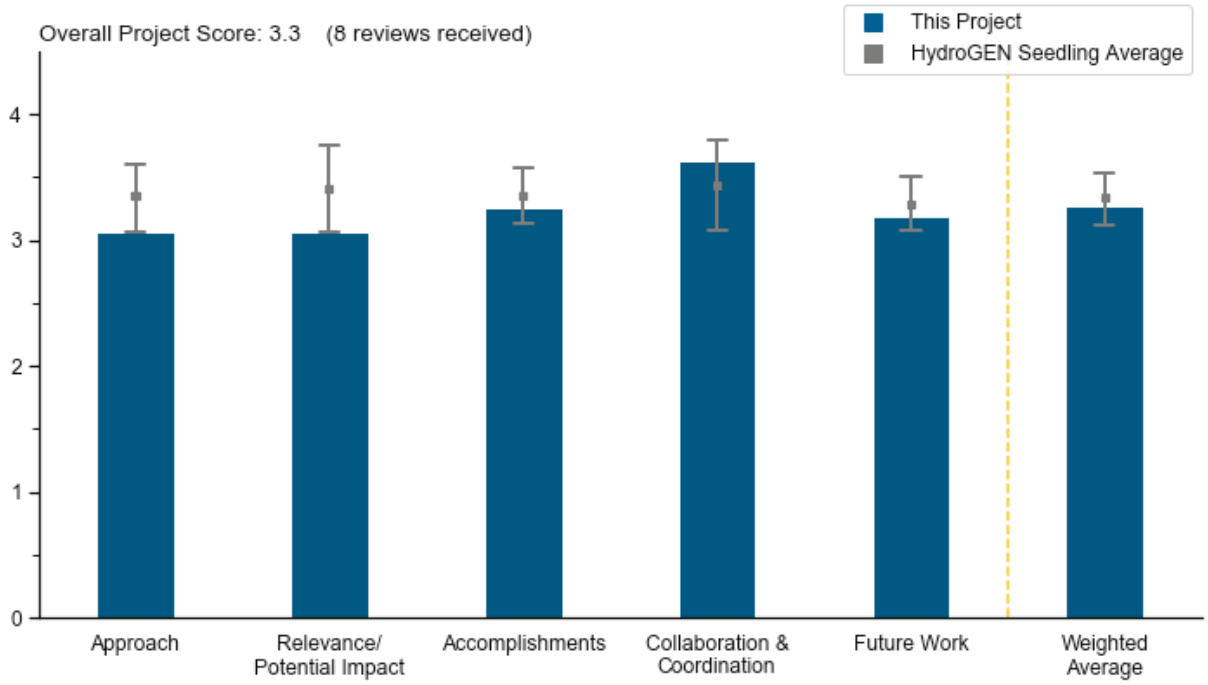
Project #P-169: High-Temperature Reactor Catalyst Material Development for Low-Cost and Efficient Solar-Driven Sulfur-Based Processes

Claudio Corgnale, Greenway Energy

Brief Summary of Project

The project objective is to develop an efficient and low-cost solar thermochemical hydrogen (STCH) process. In particular, this project is focused on the solar-driven hybrid sulfur (HyS) cycle and the development of catalytic materials to decompose sulfuric acid, a critical step in this two-step water-splitting cycle. The project will (1) develop a new catalyst material using the team's demonstrated surface free energy and electro-less deposition technique; (2) design a novel, integrated, direct solar reactor–receiver, based on a demonstrated cavity solar reactor, and (3) perform system and cost analysis on an effective new STCH plant process.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.1** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The approach is excellent. The consortium has defined its goals very well. The work performed has led to excellent results in both catalyst stability and reactor design. A comparison with the state of the art would make this work outstanding. Maybe the time limits of the presentation did not allow for this.
- The project vision is well articulated, and barriers and solutions are well explained. The well-designed project has the potential to make significant and worthwhile innovation for the HyS process. It is less clear how this project fits within the HydroGEN consortium network, and while the same (and other) laboratories are engaged as in other projects, the activities and personnel are quite different and perhaps outside the Energy Materials Network (EMN), as such. Despite this, the project is excellent collaborative work that taps into the broad expertise available within the national laboratories. The project is well constructed, with complementary activities.

- The approach of splitting the work up into three levels enables the team to focus on various aspects of the project. The barriers of each of the tasks seem appropriate and well understood. Additionally, by looking barrier by barrier, the team can focus on the individual challenges associated with each. The team is clearly highly capable of achieving the individual tasks and goals.
    - However, it is not clear that the results from each level are passed on and the needs/solutions are integrated. This seems particularly true between level 1 and level 3. Particularly concerning is the fact that the economic model identifies key operating points that are outside of the catalytic operating window, i.e., T = 875°C and P = 35 bar, when materials failure occurs below 900°C. All economic assumptions are predicated on this, and therefore new materials metrics are needed that reflect this analysis. The use of summer solstice data as the basis for economics is dubious and should be clarified or reconsidered. Additionally, the assumption/approach of using a 360-degree tower is troubling, as light distribution is unlikely to be even the entire way around.
    - Similarly, it is unclear how the collaborations move between institutions; the slides attempt to show collaboration by writing names of teams, but it seems that Greenway Energy is mostly coordinating work rather than establishing a tight collaboration. Similarly, the hub members/ consortium seem intimately integrated as project partners rather than stand-alone "helpers." A more coordinated approach should be taken in which results are more directly passed between partners. This needs to go beyond just biweekly/monthly meetings, or at least the collaborative results need to be more clearly articulated.
- This is an interesting project, and storing condensable SO_2 as a "potential" for, or deferred source of, hydrogen holds great promise as a cost-effective STCH strategy. It just seems like this project is doing too much: catalyst discovery, receiver design, plant layout, cost analysis, etc. Most of the work seems to be phenomenological in nature—or at least there is little in the way of scientific hypothesis presentation and evaluation. Many other projects and programs have looked at silicon carbide. In the U.S. Department of Energy's (DOE's) Solar Energy Technologies Office, a concentrated solar power (CSP) plant operator had a project looking at tubular SiC for a solar receiver. The researchers dropped a piece of this material on the floor from two or three feet up, and it fractured. After seeing this, they stopped investigating the material. This project does not state whether it is addressing the brittleness concern. The cost analysis does not adequately incorporate or otherwise represent uncertainty. It simply and flatly states that the cost hits \$2.0/kg H_2, which is exactly the target. It is interesting that the project suggests two significant figures (i.e., \$2.0, not \$2). The level of confidence in that 10-cent place is unclear. On slide 19, the solar plant efficiency is simply stated as 56.4, but the slide does not indicate whether this is the annual or peak average, or whether this is solar to electric or solar to thermal.
- The broader goal of the project—achieve low-cost hydrogen by developing new catalyst materials and integration with novel solar reactor design—comes through very clearly. However, the team's approach using Pt and Ir catalysts is unlikely to yield the desired goal. Besides, the project's approach is not consistent with established approaches and many other DOE-supported efforts that are trying to do away with platinum-group-metal (PGM) materials to achieve the same goal. In addition, estimating the cost of hydrogen production is not that meaningful at this time, given the early stage of development of this process, the multiple large uncertainties in the steps, and the use of PGM catalysts. This exact dilemma was part of the reason for the EMN's creation—to go back to the drawing board and focus on developing new materials.
    - The chosen configuration is very difficult to implement for multiple reasons. (1) Having a process step involving a 900°C reactor mounted on top of a 200- to 400-meter tower comes with its challenges, such as maintenance. (2) Given variabilities in weather and cloud cover conditions, maintaining a reasonable temperature gradient (and hence, conversion efficiency) across both a unit solar reactor and the entire assembly is very difficult. (3) Daily thermal swing is likely to create its own catalyst durability and capacity factor challenges unless 24-hour storage capacity is considered, which will likely have an impact on the net system cost. (4) Controlling the dual-phase H_2SO_4 flow behavior will present additional challenges.
- This project has three components to achieve the goal of developing a new STCH plant process. The project takes a very wide approach to achieve the goal. All three parts seem to be progressing well. The new catalyst level has been successful and met the milestones, but there are concerns about limited stability demonstrated (only 75 hours) and the use of PGMs. Some concerns were expressed on the reactor designs. It is unclear what happens when a cloud goes overhead.

- The basic approach is novel and compelling. However, it is not clear that a centralized tower/heliostat design is optimal. Dish concentrators may lend themselves to lower capital expenses via economies of hardware mass production.
- The project received a lower score because it seems to be evaluating many different parts of this plant vs. having a definite technical target to improve. There should be more work at the Hydrogen and Fuel Cells Program (the Program) level to determine whether STCH processes even have value. CSP is not likely viable across a large geography, and the diurnal solar cycle necessarily requires pairing an intermittent heat source with a chemical process that works better at steady state. Nuclear thermochemical makes sense, but this seems to be trying to fit a square peg into a round hole. Reevaluating the value of STCH at the Program level is recommended.

Question 2: Relevance/potential impact

This project was rated **3.1** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The HyS cycle is one of the most likely options to attain the $2/kg production cost. While not necessarily dependent on the discovery of novel materials, as is the case with the metal reduction–oxidation reaction (redox) cycles, considerable work remains necessary in the other aspects of the cycle to enable successful implementation, and this project identifies a number of these. The electrolyzer is necessarily outside the scope of this project but might be worthy of consideration within HydroGEN.
- The relevance of this is exceptionally high because cost-effective hydrogen production must occur as part of a vertically integrated industrial complex. Sulfuric acid is a foundational chemical capable of providing this opportunity. The number of process steps must be absolutely minimized and the energy recuperation maximized, where cost-effective (practical).
- This effort directly addresses the DOE goal of $2/kg H_2.
- The goal of the project is relevant to achieving an alternate low-carbon hydrogen source.
- The project supports the DOE goals. That being said, only a portion of the budget/project is dedicated to materials development. The other aspects of the project are critical to identify pinch points, but these need to feed back into the materials development to update/re-evaluate the materials' stability and performance targets. This has not been done in a sufficiently clear manner. It is worthwhile to note that the project's technoeconomic analysis (TEA) seems to show that materials development is a lower cost motivator than project location. This should be assessed and explained, as this seems to be the biggest driver of cost savings, and there is no explanation as to where the original/new locations are or why they would save $0.28/kg H_2. The project leverages HydroGEN resources, particularly for high-temperature and high-pressure testing of the catalytic behavior.
- The project is highly relevant to Fuel Cell Technologies Office objectives, and a cost-viable path to $2/kg H_2 is shown, but most of this comes from the non-technical location to increase plant capacity factor.
- It seems to be rather difficult to achieve the very ambitious goal of $2/kg H_2 using an iridium-based catalyst. The material is active, and it is stable for about 70+ hours, but the price of iridium is prohibitive for large-scale applications. Use under the very difficult solar conditions will be additionally challenging because of thermal shocks, frequent cycling, etc. Therefore, cheaper materials must be identified. The splitting of (waste) sulfuric acid is a well-developed industrial process. It would be interesting to compare the new catalyst materials with established ones.
    - The receiver design is interesting. However, it is not fully clear how the receiver will work efficiently on a solar tower with a round field. It is not clear how the receiver can be homogenously irradiated, taking into account that each mirror projects an image of the sun on the receiver that is brighter in the center and less bright at the edge. It is also not clear how the vertical flow of the gas in each fin is controlled such that the whole fin is used. Perhaps this has been solved already but was not presented in detail, probably because of limited time.
- There are serious concerns regarding the physics of the STCH pathway. Trying to pair an intermittent heat source with a continuous chemical process requires massive storage of chemical reagents and starts from behind the eight ball.

Question 3: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The consortium presented excellent developments. The stability of the materials could be improved substantially, and an interesting new reactor design was developed. The main developments in both areas are described, and patents are filed. The presentation described well how the project actions will reduce hydrogen production cost to achieve the final goal. As always, baseline cost can be discussed, but the actions to further reduce costs seem to be appropriate.
- Congratulations are due to the project for outstanding progress on the design and engineering of an innovative process cycle.
- The absence of reporting against a project plan makes it difficult to gauge progress in terms of metrics, deliverables, or timing. However, it is clear that substantial progress has been made since the last Program Annual Merit Review. The presentation shows significant progress in the solar reactor design, flowsheeting, and cost analysis. Perhaps slightly less impressive is the catalyst work, which is less sophisticated than in the other HydroGEN projects. Arguably, PGM-free catalysts are not as critical here, although the replacement of Ir is seen as important in the overall cost reduction. Good progress has been made in terms of long-term stability through use of a BN support rather than TiO_2.
- The progress on each level has been good. The project has successfully demonstrated a new catalyst that meets the requirements, showed an adequate reactor design, and conducted TEA of the reactor process. There are concerns about the cost of Ir and durability.
- The team has clearly identified and met project milestones as originally outlined, and the data appear convincing in terms of catalytic activity and longevity. The team presents system efficiency numbers that achieve the milestones, but these are less substantiated. Based on the data, it is imperative that the milestones and future go/no-go's are based on updated catalytic stability numbers that reflect the required operating conditions of the plant (T = 875°C and P = 35 bar)—harsher conditions than those under which the materials failure occurs. The budget looks appropriate for the work done, but no budget was presented for the second time period.
- There have been significant accomplishments toward catalyst development that exceeds targets. Perhaps this would be useful in nuclear thermochemical.
- It appears from the presentation that the project met its stated milestones. However, it is difficult to verify some of the assumptions that led to the optimistic results. For example, the solar-to-electric efficiency for a similar but simpler and more established tower-based direct-steam design for CSP is about 21%, which suggests even lower solar-to-hydrogen efficiency than the results shown in this project. The presentation material did not make the project resources or funding level clear, which would help in better gauging the accomplishment. The stated funding is for year 1 funding, and year 1 started September 2017.
- For the budget and the time elapsed, the accomplishments are okay; however, there are too many things happening, and so each accomplishment is less than excellent. For example, an interesting catalyst has been identified, but it comprises PGMs. An interesting receiver design has been proposed, but it is built of very risky materials. A cost analysis is complete, but it does not include error bars or some assumption analysis.

Question 4: Collaboration effectiveness

This project was rated **3.6** for its collaboration and coordination with HydroGEN and other research entities.

- This project plays a key role for HydroGEN, as it is the only one that takes the application of the process heavily into account. The exchange within HydroGEN seems to be excellent. The data provided for the Data Hub is of especially high value, as it helps the other HydroGEN projects to get a sense of how their processes might get implemented on solar tower facilities and how flowsheets of such processes would look.
- This is a very diverse and innovative team. The results, patents, publications, and presentations are evidence of outstanding collaboration and coordination.

- There is very good collaboration with HydroGEN partners, including Idaho National Laboratory for testing, the National Renewable Energy Laboratory (NREL) for reactor modeling, and NREL and Savannah River National Laboratory for TEA.
- The project is well coordinated and effectively leverages the appropriate expertise at institutions both inside and outside the EMN. Collaboration is happening and is well documented.
- The collaboration effort of the project team looks excellent, including the use of the HydroGEN Advanced Water Splitting Materials nodes.
- There is great collaboration across national laboratories and universities. It would be good to see a company or end user that would like to develop this technology to buy down risk on the application side.
- It is clear that the use of the nodes is critical to the work of this project. Hydrogen partners appear to do a great deal of work that has led this project to meeting its goals, particularly in terms of materials testing. There seems to be little integration with the 2b benchmarking and protocols team, the cross-cutting project, etc. The use of the Data Hub seems to be as a repository for work but not of great materials-sharing or development data value.
- Collaboration is good, but with so much of the work being delegated, it seems the results should be more robust.

Question 5: Proposed future work

This project was rated **3.2** for effective and logical planning.

- The proposed future work is completely logical. This is the way to proceed. It is very likely that the proposed way will lead to excellent results that help to implement the technology.
- The project appears well managed, with a good understanding of where it is and what the next steps need to be.
- The proposed future work is good and seems to have recognized some of the potential barriers (such as stability and cost) that need to be addressed. There are still open questions related to stability and long-term durability that need to be addressed.
- The future plans reflect the massive body of work that lays ahead.
- This is appropriate; however, materials requirements need to be updated to reflect the operating conditions found by systems modeling.
- The proposed future work all seems appropriate, but it seems to be continuing along the vein of trying to tackle too much. The project should identify the truly enabling aspect of this technology and focus on doing that bit first—and very well—and then tackle subsequent areas.
- The project team should focus on developing non-PGM catalysts and put less effort into system TEA. The new catalysts can potentially be used for other non-solar-based configurations. Since the current catalysts are unlikely to deploy commercially, it does not make sense to spend time on long-term durability tests.
- It is not clear what the next steps would be. Catalyst development is the highest-value target but is worth only a 7¢/kg cost reduction in the waterfall chart.

Project strengths:

- The global view on the whole process is the major strength of the project. The achieved results help with understanding the key components of the process, the active catalyst materials, and the solar reactor. Flowsheeting is used to describe the whole process and can be used for a sound economic evaluation.
- Strengths include very strong catalytic work and modeling/system design across different levels of the project. This project stands out in offering an approach to STCH different from other projects in terms of technology and systems design.
- The team is focused and making excellent progress toward a challenging goal. There are excellent collaborations within HydroGEN, and the team has made efforts to ensure good communication around the different parts of the project.
- The project team all have experience in the respective areas. The principal investigator is ambitious. The chemicals employed are of importance on national and international scales.
- This is an impressive piece of work that effectively utilizes the multi-institution competencies both within and outside the EMN.

- The ability to innovate is the team's most obvious strength. The involvement of commercialization partners is an area of strength that is missing from many other STCH projects.
- A strength is the ability to coordinate diverse skill sets, namely catalyst development and reactor and systems modeling.
- The project has good technical work.

Project weaknesses:

- There is a question of fit to the HydroGEN consortium, but in the absence of an alternative, this project should continue to be funded here.
- The selected materials seem to be too expensive and too rare for an application in the gigatonne range (which will become the hydrogen range). A comparison with the state-of-the-art catalysts would show whether this weakness might be overruled by the improved efficiency. The reactor design needs a deeper description concerning annual operation on a solar tower and flow within the receiver. Probably this was already done, but it was not presented in sufficient depth, probably because of time restrictions.
- If the project moves forward, getting some commercial catalyst and system original equipment manufacturers (OEMs) involved would be helpful. Boron nitride and silicon carbide are both commercially made and manufactured. OEMs should be able to help with understanding thermal cycling's effect on these catalyst supports.
- Better team integration is needed across the levels in terms of updating system results and moving new operating points. The reactor model needs to be updated to include shape factors and consider the implications of hot spots on the feasibility.
- The project team appears to downplay or ignore multiple significant technical challenges, which potentially led to the oversimplification of the technoeconomic model.
- A weakness is the apparent absence of risk management plans that address uncertainties involving the novel reactor design.
- There is a focus on PGMs that may limit applicability, and durability has not been adequately addressed.
- The project is trying to tackle too much all at one time.

Recommendations for additions/deletions to project scope:

- The project is excellent. It is on the right track. The project goals should be kept as they are.
- It would be valuable to have some harmonization of target performance across the HydroGEN projects. Each project has its own targets that could benefit from some inter-comparison to ensure that each set is sufficient to meet or approach DOE targets. All the HydroGEN project presentations should be made clearer in terms of the project plan and performance against the expected timeline.
- The project should focus on material identification, evaluation, and selection for the solar receiver and the design. If there are no materials that can operate with an adequate chemical, mechanical, cost, and risk profile, then that needs to be addressed.
- The value of STCH should be re-evaluated from a Program perspective, and risk should be mitigated by adding an end user. Involving catalyst, support, and OEM companies would buy down development risk.
- Materials stability requirements need to be updated per the system model; they do not account for the harsher operating conditions that are required.
- Non-PGM and durability focus should be increased. Given the emphasis of HydroGEN, the team should reach out to the EMN to better understand the catalysis mechanisms.
- The team should focus on catalyst material development, the basis for subsequent reactor and system studies.

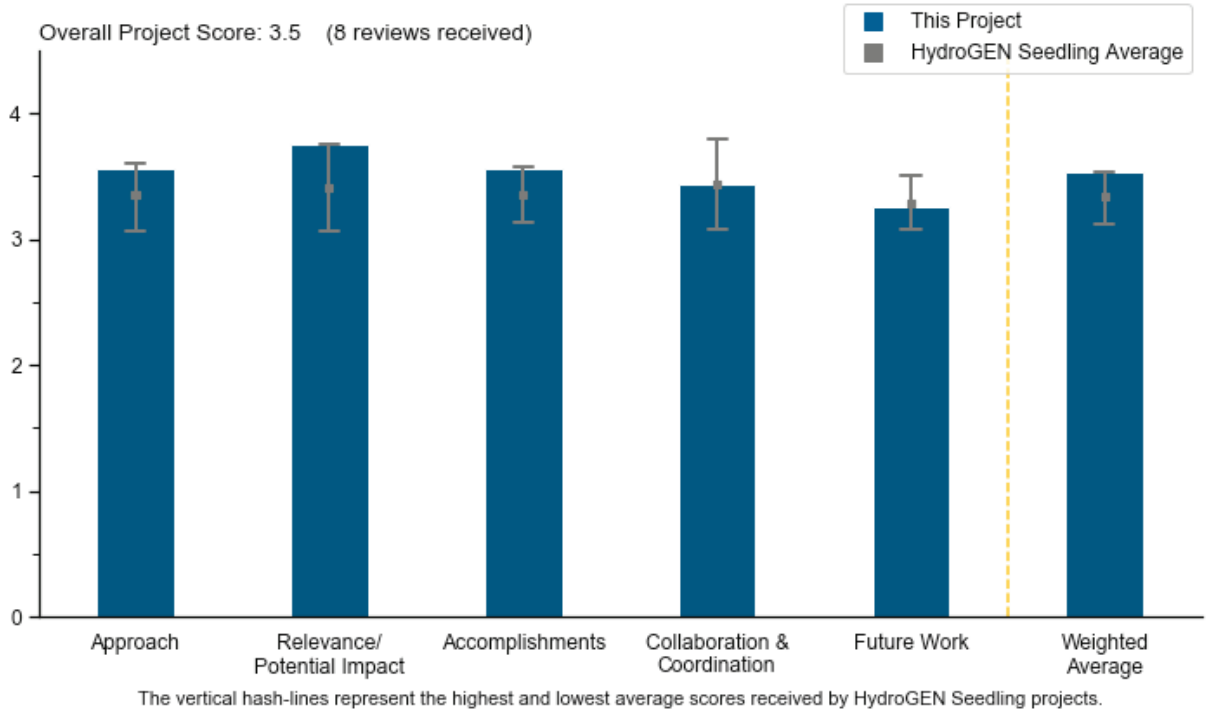
Project #P-170: Benchmarking Advanced Water-Splitting Technologies: Best Practices in Materials Characterization

Kathy Ayers, Proton OnSite

Brief Summary of Project

The project will develop a community-based living roadmap across technologies to assist in maintaining a balanced U.S. Department of Energy (DOE) portfolio. The project vision is to (1) develop a cohesive research and development (R&D) community working together; (2) interact with the Energy Materials Network (EMN) to define targets, best practices, gaps, and priorities; (3) aggregate and disseminate knowledge; and (4) accelerate innovation and deployment of advanced water-splitting technologies. The assembled team of subject matter experts for each sub-area will engage with each sub-community. A consultant from a similar effort in hydrogen storage will convey lessons learned. The project addresses a lack of consensus regarding testing protocols and standards and the need for a large diversity of information for compiling and developing. The project also addresses challenges presented by differences in technology readiness levels (TRLs) between different technologies.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.6** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- The development of standards and protocols for benchmarking is critical for providing an "apples-to-apples" comparison tool, which will allow researchers to evaluate and compare the performance of their materials relative to DOE technical targets. The development of protocols for benchmarking durability is challenging, given the goal of predicting long-term durability using a short-term test metric, but it will be of great value in the long run if an appropriate protocol can be developed and validated. The project appears to be well designed and well managed. The project includes non-HydroGEN members, both domestically and internationally, to gather information and feedback to develop the benchmarking protocols; this inclusion

could allow the developed protocols to serve as the benchmarking metrics for the entire global scientific community.

- This is a good approach, given that the broad-ranging project covers benchmarking for three diverse water-splitting technologies. The metrics and survey priorities are a logical start to gathering information. Assembling roadmaps will give a high-level overview and enable better communication across the different hydrogen production options. Identifying gaps should allow for more strategic application of funds. Establishing standardized benchmarking protocols for testing should lead to better definitions of protocols and support the overall knowledge transfer.
- Addressing the need for such a database and roadmap is a very good idea. Gathering a community of experts to establish a set of protocols is of great value; the ability to compare developing components and emerging technologies is key to comparing various research groups' results. The searchable library of current protocols, procedures, and data is a great means of accessing the field.
- The approach for the project is reasonable. The team understands community acceptance is of utmost importance when developing protocols and has established methods to listen to the community through meetings and surveys. Identifying gaps and proposing future development roadmaps ensure the continued development of the initially proposed protocols.
- This is a large, intractable project that requires a high degree of collaboration. The structure of a lead principal investigator (PI) (and co-PIs) leading multiple subject matter expert entities is perhaps the only feasible approach. The community must accept the approach, so there must be significant industry input in development of the metrics. Given the wide scope of the project, breaking the project into five tasks, with sub-tasks for each technology, is a practical way to manage the project. A quarterly newsletter is an inefficient way to ensure interaction among stakeholders (or at least awareness of issues).
- The approach is very nice and systematic in terms of looking at different critical issues. There could be more outreach to international organizations in terms of the questionnaires and utilizing work being done by the International Energy Agency, etc. The technologies are all at different TRLs, and so the approach needs to be tailored a bit more for that. The audience of the protocols is unclear, as is how they will be utilized or validated.
- The project team has a comprehensive and well-thought-out approach for developing a framework for testing protocols and accumulating standards for water-splitting materials and associated pathway technologies. The researchers are using their own considerable expertise in conjunction with mechanisms (e.g., survey/questionnaire and in-person workshop) used to elicit input from the larger research community. This said, it is not completely clear how "best" practices will be assessed as such, or what metrics should be used that reflect how effectively the team is facilitating acceptance of community-wide technology.
- This is an ambitious effort, with many moving parts and reliance on building trust networks with various technology development communities outside HydroGEN. Given the limits on budget and time, this effort should focus its resources on (1) developing and documenting protocols, standards, and testing methodologies; and (2) building consensus and acceptance within respective communities for those outcomes. The roadmap and gap assessment activities, if necessary, should be conducted elsewhere.

Question 2: Relevance/potential impact

This project was rated **3.8** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- The collaborative input and participation of government, industry, and academia are important for a clearer understanding of practical needs for the technology and the current state of the technology. Management and analysis of these stakeholders' responses to surveys, etc., are of significant importance. Care must be taken not to have bias toward one group or technology, so it is key to get the biggest pool of responses for each questionnaire and survey. It is acknowledged that the PI is at the mercy of the participants' schedules and willingness and ability to submit feedback in a timely manner. However, slide 9 shows that a total of only 70 questionnaires were sent, which seems to be a small set.
    - The development and open dissemination of test protocols to interested parties could ensure that measurements, test conditions, etc. are all consistent and directly comparable. The collective results of this project could greatly reduce the time researchers need to develop their own

protocols. Many accomplishments are provided, including holding workshops; developing, disseminating, and collecting questionnaires; developing several standardized tests; and doing calibrations.

- The development and validation of benchmarking standards and protocols that are accepted by the broader scientific community is critical to supporting and advancing R&D progress toward meeting the DOE Fuel Cell Technologies Office (FCTO) and HydroGEN EMN overarching goal of producing hydrogen from renewable energy sources at a production cost of \$2/kg H_2. The project does a good job leveraging the capabilities and expertise within HydroGEN to develop and execute benchmark protocols and standards, but the team also recognizes the need to engage the broader scientific community.
- Standardized testing will be critical to helping DOE bring diverse stakeholders together. Testing will also provide realistic input to Hydrogen and Fuel Cells Program goals and give clear, quantitative benchmarks to show whether future efforts are actually making progress toward cost and performance goals. Of great interest is the potential for reduced development cycle timelines and better management of R&D funds.
- This project brings a critical element to the HydroGEN consortium by ensuring that the methods used to discover and validate new water-splitting materials are used consistently across the research community. This type of benchmarking is rare and addresses issues of validity and provenance of data while this sub-field of materials science and engineering is still gaining maturity.
- The project has high relevance. Common frameworks and definitions are required for the clear discussion of ideas. DOE is uniquely capable of organizing this effort. Project outputs clearly benefit that community and the nation.
- This is a well-needed area and activity that FCTO should be doing. The impact could be very large, although that will vary with the technology level—with lower TRLs perhaps benefitting the most.
- A standard and fair comparison for the different water-splitting technologies has been a need in the community for years.
- Congratulations are due to the team, who accomplished quite a bit in the first year.

Question 3: Accomplishments and progress

This project was rated **3.6** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- There has been good progress to date in engaging both the HydroGEN members and the broader scientific community through the workshop (annual project meeting), questionnaires, and face-to-face discussions to define the needs and developmental pathway for establishing the benchmarking protocols and standards. The node gap analysis is critical to determining whether the required capabilities and expertise exist and are at the appropriate readiness level within HydroGEN, or if there is a need to leverage outside capabilities and expertise within the DOE national laboratory system—those not already involved in HydroGEN—or the broader academic or industrial community.
- This is a large project for which consensus may be difficult to achieve. Nonetheless, it appears substantial progress has been made. Technology roadmaps appear to be key and very useful products of the project. Roadmaps have been drafted but have not yet been finalized. A first round of test protocols has been developed. From the number of protocols, it appears to be a very substantial body of work.
- The project has completed five of six milestones, with a final go/no-go decision under discussion. The draft roadmap has been completed for each technology area and now should have some level of external third-party review from sources not involved with DOE or the national laboratories.
- The accomplishments are documented and are impressive. If participants and the research community contribute to the DOE database, it will be a great asset to all.
- By its very nature, if this project did not collaborate and build trust networks with HydroGEN and the broader technology development communities, it would fail. Thus far, it does not look like a failure.
- The team has made really good progress in the past year.
- The team has an impressive list of accomplishments for the amount of time spent so far on this effort (roughly one and a half years). The list includes the creation, distribution, collection, and analysis of questionnaires for each water-splitting pathway, development of a test framework, analysis of nodes (capabilities) missing from the HydroGEN consortium and needed for materials discovery or validation, a community-wide workshop, definition of an initial set of test protocols across the water-splitting pathways,

and creation of draft roadmaps for these pathways. One element that seems to be missing is publications that bring methodologies and results developed in this project to the wider community. A majority of the items listed on slide 26 are conference presentations and (perhaps) proceedings. However, increased impact will be achieved by even wider dissemination of the team's results through peer-reviewed journal articles.
- The team has made progress in defining and getting input from stakeholders and defining what needs to be done in terms of the protocol development. The maps and initial outputs are promising, as was the workshop, but the exact follow-up is not clear. Also, the pathways are not easily translatable among the different technology pathways, as they exist at different levels.

Question 4: Collaboration effectiveness

This project was rated **3.4** for its collaboration and coordination with HydroGEN and other research entities.

- A strength of this project is its effort to engage the broader global scientific community to assist in the design, development, and validation of the benchmarking standards and protocols. It was particularly encouraging to see the high level of response from the international community, as shown in the table on slide 9. Developing benchmarking protocols and standards that are accepted by the broader scientific community will go a long way toward accelerating the development of the renewable hydrogen production technologies being pursued by DOE and HydroGEN, which could provide added benefit to DOE.
- The project appears to be have been highly effective in collaboration. A large number of industry experts have been involved, with numerous opportunities for researchers to voice their thoughts. The regularly scheduled meetings, use of questionnaires, and breakdown into technology-specific topics all combine to create a highly collaborative work environment.
- Developing protocols is difficult; the project team seems to engage the HydroGEN and larger community with all the steps along the way.
- Advising about standard practices, as well as having a means to compare disparate results against standards, is very important for advancing R&D. This is an ambitious effort with potential for high impact.
- This group has done a great job engaging, collaborating, and coordinating with many groups in the field.
- The team is doing a great job at collaborating and coordinating the core team's individual areas of expertise to lead community information-gathering efforts in these areas. The team is still in the process of consolidating the different contributions for dissemination on the Data Hub website, and thus the appearance of the site is very rough and provides only questionnaires and results at this time. According to the PI, many of the additional contributions (e.g., test protocols) are available on the primary h2awsm.org site. Consolidation onto the Data Hub will be critical; it will limit user frustration and maximize accessibility. At the least, the Data Hub should contain links to this other information. It would also be good to see a more detailed list of the institutions (outside of HydroGEN and the benchmarking team) that are contributing information used for this activity. This would provide a sense of how large the affected and participating community actually is.
- Outreach to the community has been good, although further international participation would be good, as would ensuring that the protocol audience members are participating. Collaboration with companies that work with similar technologies such as fuel cells, chlor-alkali, etc. would be good as well.
- With the diverse maturity levels, it may be difficult to find sufficient collaboration from industry. It would be helpful to have a separate listing of all external review efforts for each individual advanced water-splitting technology: electrolysis, high-temperature, and photoelectrochemical (PEC). A limited number of partners outside of the laboratories or FCTO were mentioned.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- Developing protocols for evaluating durability and degradation is a challenging but extremely critical task. The assumption is that sub-scale development is focused on establishing benchmarking protocols for components and systems at the pilot scale. Given that this appears to be a two-year project slated to end at the end of fiscal year 2019, it is unclear whether this effort is part of Phase I or work that will be done if the

project is renewed. Developing benchmarking protocols for components and systems is as critical as developing benchmarking protocols for materials and should be pursued, whether it is part of budget period 1 or budget period 2 (presumably budget period 2 is the renewal). The node gap analysis identified the need for node expansion in each technology. This appears to be a critical issue, and if so, it is unclear how these needs will be addressed: perhaps this work can be done with existing capabilities and expertise within the six national laboratory partners, or perhaps it will require external collaboration, either within or outside the DOE national laboratory system.

- While the project is ending in September 2019, there are several important items listed as proposed future work. If any or all of these items are completed, this would have to be considered a very successful effort.
- Several milestones are left for 2019, and the list of operational conditions, accelerated testing protocols, and gap analysis will be critical to leveraging existing work to date.
- Development of accelerated testing protocols is particularly noteworthy. A future focus on bench-scale validation is also well considered.
- Future work shows a clear path forward.
- This group and the associated HydroGEN laboratories will be quite busy developing, testing, and validating protocols (at whatever scale). Assessing the capability content of HydroGEN and identifying gaps for future needs should be conducted separately from this project.
- The dissemination strategy, and whether information will reach everyone it needs to, is not clear. DOE might have to drive this. A critical step in this activity seems to be protocol evaluation and verification, which is not budgeted or handled by this group, but it seems the EMN nodes might handle this step—that is not clear or budgeted. This is the main reason for the lower score given. It is not clear how the outputs of the first workshop are being used, especially for subsequent workshops, which are proposed to be annual. The proposed work in terms of approach is fine for the protocol development, aside from the comment regarding validation, which is a final milestone.
- The proposed future work presents a logical sequence of next steps needed to formalize this protocol development. It is curious that the milestones for budget period 2 do not mention specific deliverables associated with disseminating the team's results and accomplishments. It is not clear if there is a plan for this beyond feeding data into the Data Hub.

Project strengths:

- The establishment of benchmarking protocols and standards for materials, components, and systems is critical for enabling DOE to meet its hydrogen production cost target. The engagement of the broader scientific community in developing the benchmarking protocols and standards is a particular strength of this project. This engagement has the potential to have these protocols and standards accepted by the broader scientific community (beyond HydroGEN), which could benefit DOE in the long run by accelerating the development of these technologies.
- The PI, Kathy Ayers, is very well suited—perhaps uniquely suited—to lead this effort. She is a key strength of the entire project. The team of subject matter experts selected and willing to participate is another strength. They collectively represent the cutting edge of the relevant technologies. This group's adoption of the final test protocols will ensure adoption of new standards throughout the community—and the world.
- This project brings a critical and valuable element to the HydroGEN consortium's activities. The approach is comprehensive and well thought out, and it is producing results that further the goals of DOE, HydroGEN, and the larger water-splitting materials community.
- This ambitious effort is heavily predicated on successful engagement with HydroGEN and the larger technology R&D communities. Thus far, the approach appears sound and is producing results, thanks to the strength of the core project team.
- The strength of this project is having identified the need to establish a set of standards for evaluation in a specific technology. The team has systematically engaged the experts; collected and analyzed their thoughts, opinions, and inputs; and produced agreed-upon protocols.
- This is a critical area with a good team across different technologies. The project has a very systematic approach toward establishing roadmaps and benchmarks but can work with others doing similar efforts in related technologies.

- The project involves a diverse group across academia and industry. This is a quantitative effort, with standardized surveys requesting status and updates of the three different hydrogen production areas.
- This is a well-thought-out and much-needed project for the community. The main strengths are in the accomplishments so far, as well as the open communication with the stakeholders.

Project weaknesses:

- In looking at the limited information provided in developing the benchmarking protocols and standards, there appear to be a significant number of properties for which protocols and standards are being developed for new materials being developed for a specific technology. There is a very high probability that a new material will not meet all of the required performance targets. It is not clear whether there is any effort or benefit to ranking which material property is most important at the early stage of development. Such an effort might serve as a guide to help both developers and funding agencies determine whether a material should be further developed and, if so, where the R&D focus should be.
    - Given that this project is still in the early stages of defining and developing the protocols and standards, there are no glaring weaknesses. Critical will be the validation and acceptance of the protocols and standards. The perceived value of the project is extremely high. The more difficult task will be trying to "quantify" the benefit in terms of how it accelerates and reduces the cost of technology development.
- Perhaps the initial questionnaire pool was too small, but otherwise, this is an important project.
- There are no significant weaknesses that need mentioning.
- Protocol validation is critical but not within scope. The effort and the approach are being applied equally among the technology pathways, although the lower-TRL ones should need some more effort than the higher-TRL ones, or perhaps a different focus. Also, the PEC ones, for example, can leverage previous activities, whereas high-temperature electrolysis can perhaps leverage solid oxide fuel cell efforts and low-temperature electrolysis can leverage company efforts. It is not clear how these are being translated and whether the gaps are being identified with that perspective in mind.
- It is unclear how "best" practices will be assessed as such, or what metrics should be used that reflect community acceptance of water-splitting materials and technology. One element that seems to be missing is publications that bring methodologies and results developed in this project to the wider community, thereby increasing its impact.
- This effort should focus its resources on (1) developing and documenting protocols, standards, and testing methodologies; and (2) building consensus and acceptance within respective communities for those outcomes. The roadmap and gap assessment activities should be conducted elsewhere.
- The project could use additional industry or objective third-party input on the effort.
- Frameworks and roadmaps are not yet finalized (they are behind schedule).

Recommendations for additions/deletions to project scope:

- The project scope seemed ambitious but appears to be going exceptionally well, based on the demonstrated accomplishments. No additions or deletions are suggested.
- Once the benchmarking protocols and standards are established and are being practiced, there should be a follow-on effort to evaluate the effectiveness toward accelerating technology development to meet DOE's overall goal in terms of its hydrogen cost target. Developing protocols and metrics for benchmarking material performance typically utilizes commercial analytical equipment for conducting the evaluation; most materials developers either own such equipment or can easily get access to it. For components and systems, standard commercial breadboard-type systems either do not exist or are not readily accessible to many developers, especially those developing components. Component developers often use computer-based engineering systems modeling and analysis to evaluate component performance and its effects on system performance as a means of reducing cost. The team should consider engineering systems modeling and analysis as a tool for benchmarking performance in an integrated system.
- It is critical to consolidate information to the Data Hub, so that all project results are in a single "location." Also needed is a more detailed list of institutions that are contributing information to this activity, as it would provide a broader sense of the community size invested in this research field.

- International reviews of the roadmaps and additional input or review of progress would be helpful, if resources and time allow.
- It appears likely that follow-on work to update, expand, and further validate the frameworks and protocols will be beneficial.
- The project needs to add validation of protocols, which should be done at the HydroGEN laboratories.
- The project should delete the technology development roadmap and EMN capability gap assessment activities.

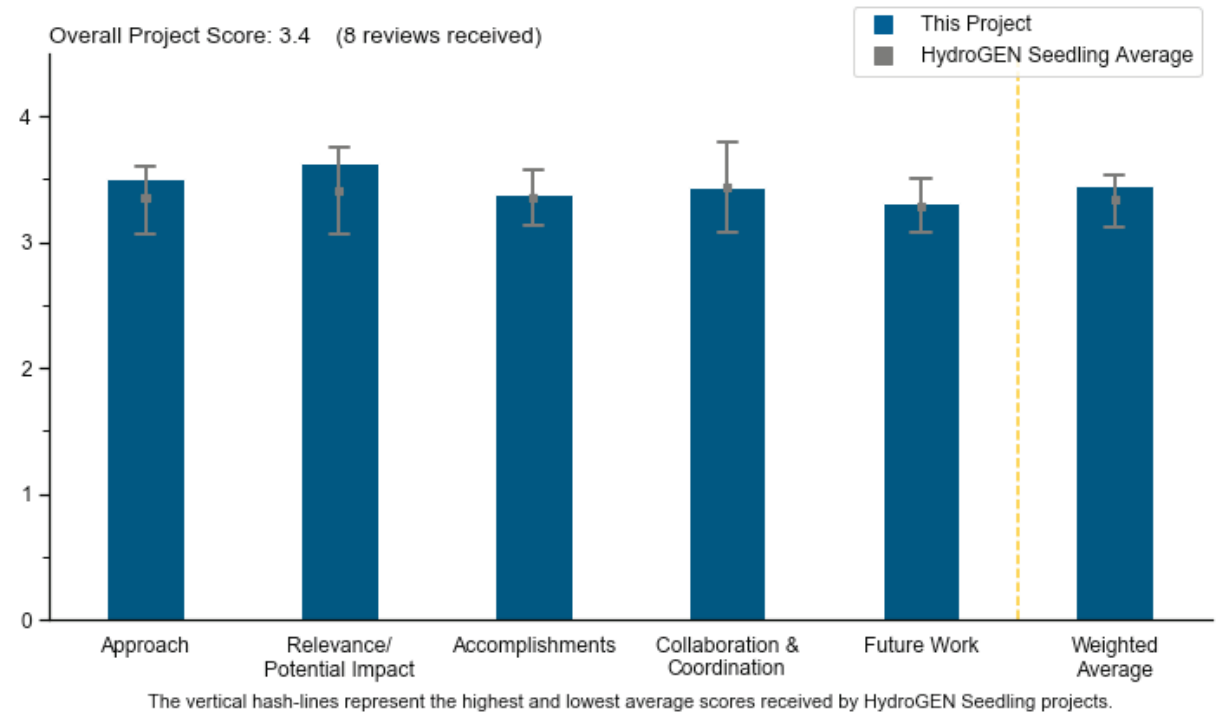
Project #P-175: Intermediate-Temperature Proton-Conducting Solid Oxide Electrolysis Cells with Improved Performance and Delivery

Xingbo Liu, West Virginia University

Brief Summary of Project

This project will develop an intermediate-temperature proton-conducting solid oxide electrolysis cell (H-SOEC) through innovative material discovery, high-throughput screening, and model-informed electrode design. The result will be an anode with extensively broadened reactive sites and highly intrinsic electrocatalytic activity to yield current densities in an H-SOEC of >1A/cm^2 at 1.4 V/cell at 600°C and degradation of <4 mV/1000 h. The team will identify highly active, triple-conducting electrocatalysts and develop conformal coating methods for depositing these catalysts into composite anode functional layers to lower the dominant anode polarization resistance associated with water splitting in H-SOECs.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.5** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- There is no need to improve any more. The proposed approaches can effectively fulfill the U.S. Department of Energy's goals.
- This is a strong project with a solid team and several excellent concepts that are being pursued. The project has the very good idea of simultaneous water splitting and hydrogen separation to suppress nickel oxidation, and the coefficient of thermal-expansion-matched anode and electrolyte materials are good ideas if the performance of both the electrolyte and anode materials can be optimized. There are some compelling reasons to consider proton-conducting ceramic electrolytes for electrochemical water splitting to produce hydrogen. Operating temperatures are high enough so that precious metal electrodes are not required, yet not so high that thermal integration is challenging. The electrode-supported electrolyte membrane architecture targeted in this project makes a lot of sense for minimizing resistance (and power

consumption) during electrolysis. A challenge is that the best proton-conducting ceramics (based on barium zirconate) require very high sintering temperatures for densification, which makes it difficult to achieve the targeted porous-electrode-supported, dense-thin-film electrolyte architectures. Another challenge is that the design of electrochemically active and stable electrode materials for operation at 600°C is not easy.

- The researchers are addressing the key issues and, unlike many others in the proton-conducting field, are considering the impact of potential nickel oxidation. They are using experiments and modeling to understand the system. They are proposing atomic layer deposition for the catalyst. It is not clear that this deposition approach can be economically scaled.
- There is a good balance of experimental and modeling contributions to address the project's objectives. There is a worthy objective of increasing the durability of high-temperature electrolysis by moving to a proton-conducting system that can operate at somewhat lower temperatures. One caution is that the approach involves a large number of challenges; the team should make sure to focus on few enough of them that meaningful progress can be made.
- Addressing interfacial conductivity to solve some of the proton-conducting solid oxide electrode issues seems to be a promising approach.
- A triple-conducting backbone electrode offers substantial theoretical advantages for SOEC systems.
- The approaches are logical and appropriate, considering the current stage of development of the technology.
- The presenter answered questions clearly. The project focused sharply on overcoming critical barriers and presented strategies to address the issues.

Question 2: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- Solid oxide electrolysis is a key component of DOE's emerging portfolio of hydrogen production technologies. If this project is successful, a promising materials set for SOECs with potential for improved long-term durability will be identified for the future development of SOEC stack and system technology. Thus, this project has high relevance and a significant potential impact.
- The project brought in a new concept and characterization for achieving high-performance, high-temperature electrodes for efficient and cost-effective hydrogen production. It is critical to the DOE Hydrogen and Fuel Cells Program (the Program) and has the potential to contribute significantly to DOE goals and objectives; the project is significantly leveraging and contributing to the HydroGEN consortium.
- Intermediate-temperature electrolysis is a key enabler for H2@Scale and is very relevant. Since the electrolysis occurs at an elevated temperature, significantly less electrical power is required compared to low-temperature electrolysis, which translates into lower-cost hydrogen. The project is using low-cost materials, resulting in low capital costs. The researchers are trying to decrease the degradation rate, which is a key limiter for high-temperature electrolysis.
- The project aligns well with the Program and DOE research, development, and demonstration (RD&D) objectives, and it has the potential to advance progress toward DOE RD&D goals and objectives.
- The project is likely to uncover important information to guide further development of hydrogen SOEC technology.
- The direct separation and potential electrolysis of hydrogen is highly relevant; this characteristic advantage seems understated.
- The project aligns well with the Program.
- The project is relevant to high-temperature water electrolysis.

Question 3: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- Within the short term of the project period, the team has achieved very good current density under -H-SOEC mode and has produced three papers or manuscripts. This project is on the right track to approach its objectives and make significant progress toward overall DOE goals.
- The project started in fiscal year (FY) 2019. Key research thrusts that have started include developing the system model, exploring the material composition space using high-throughput screening, synthesizing and characterizing new materials, and doing button-cell testing.
- Excellent progress toward the project objectives has been demonstrated through clear and measurable performance indicators; the results suggest that one or more critical barriers will be overcome.
- The project goals are on track, with good progress made on model development. Evaluating conditions (such as water concentration) should be stated on the target table for the various years.
- This project just recently started, so it is difficult to judge progress. Some materials issues have been identified, and good progress has been made to address them.
- Progress has been made toward achieving the overall objectives.
- The project has made sufficient progress.
- The kinetic model development is very good and will be useful in modeling a cell or stack. The project achieved the ~1 A/cm^2 current density at 1.4 V and 700°C. The temperature is very high for an "intermediate" temperature stack. It would be expected to be closer to 600°C. The researchers will need to improve their catalyst. The durability was done at the very low current density of 400 mA/cm^2, so it is not surprising that they were able to meet the durability target. To evaluate the durability, they need to stress the cell by operating at higher currents. The fabrication methods being used are not very amenable to stack fabrication.

Question 4: Collaboration effectiveness

This project was rated **3.4** for its collaboration and coordination with HydroGEN and other research entities.

- The collaboration between West Virginia University (WVU), the Colorado School of Mines (CSM), the National Renewable Energy Laboratory (NREL), and Idaho National Laboratory (INL) is perfect. They all contribute to the project well. If regular team meetings could be scheduled, it would be better.
- This is a strong team, and there appears to be a high degree of collaboration among the team members. There seem to be many moving parts in this project; it will be interesting to see how they all come together.
- There are effective collaborations with partners. Using NREL to do combinatorial studies is interesting. It would be good to see how those studies are being done and the results. Combinatorial studies are difficult to set up to ensure no false positives or negatives are produced. Unless the testing is being done in a relevant environment, misleading results may occur.
- All research thrusts (WVU, CSM, NREL, and INL) are engaged and contributing to the objectives laid out in the plan.
- There has been excellent and effective coordination between the team members.
- It appears that collaboration between partners is well coordinated.
- The interactions between collaborators are reasonable.
- Collaboration appears effective and extensive.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The future work seems to be well planned. The proposed tasks are effective for overcoming most of the technical barriers.
- The proposed future work is excellent. If there were a plan for integrating the X-ray photoelectron spectroscopy (XPS) characterization results with the electrode kinetics model, it would be better.

- The proposed future work is a logical continuation of the presented effort. Hydrogen cost and thermal cycling should be part of future testing.
- There is a reasonable outline of the next steps. It would be good to see some modeling added to guide materials composition selection.
- The researchers are focusing on improving the performance and addressing the key challenges. They should consider the manufacturing aspects of how to scale up the cells or work with someone who has experience in stack manufacturing.
- The proposed future work is appropriate to address the identified technical barriers.
- The proposed future work is consistent with the project objectives.
- The FY 2019 combinatorial catalyst-coating task should conclude or be constrained before the start of FY 2020 to avoid changing too many variables going into the conclusion of the project.

Project strengths:

- The project integrates the kinetic modeling, button-cell evaluation, materials screening, in situ XPS characterization, and large-scale testing, allowing for significant achievement. The new design and understanding of a triple-conducting composite anode will significantly boost research in the high-temperature electrolysis field. The use of "environmental" XPS (E-XPS) is also a great addition.
- The breadth of the team and the approach are strengths, as is the extent of progress that has been made in a short period of time. The team is working on an important challenge (durable steam electrolysis systems).
- The project has a strong team. Strong concepts are being evaluated. New materials sets are being established with the potential for high performance and long-term durability.
- The project has excellent kinetic modeling capabilities and a good team. The materials are of interest and have the potential to achieve their technical targets.
- The project has a unique approach that, if successful, is well suited to meet DOE goals and targets.
- The project is focused on addressing the interfacial transport of various species.
- The project's main strengths are the approaches for addressing the technical issues of the proposed concept.
- The team seems to work together well.

Project weaknesses:

- The project has no major weaknesses.
- The durability is in question since the tests run were at a very low current. The button-cell fabrication techniques are not amenable for large cell and stack fabrication.
- The researchers may be biting off more than they can chew, so it may end up being difficult to generalize or build off of the results.
- With so many moving parts, maintaining focus and team cohesion will be a challenge.
- There are several opportunities to get stuck in an "optimization loop" as the project concludes.
- The efficiency of the proposed system is not mentioned.
- The coatings might be more prone to fracturing.

Recommendations for additions/deletions to project scope:

- It is suggested that the team do the durability testing in a lower steam concentration (below 60%).
- The durability tests should be done at a more challenging current.
- The team's materials modeling capabilities should be considered.
- There are no recommendations for additions/deletions to the project scope.

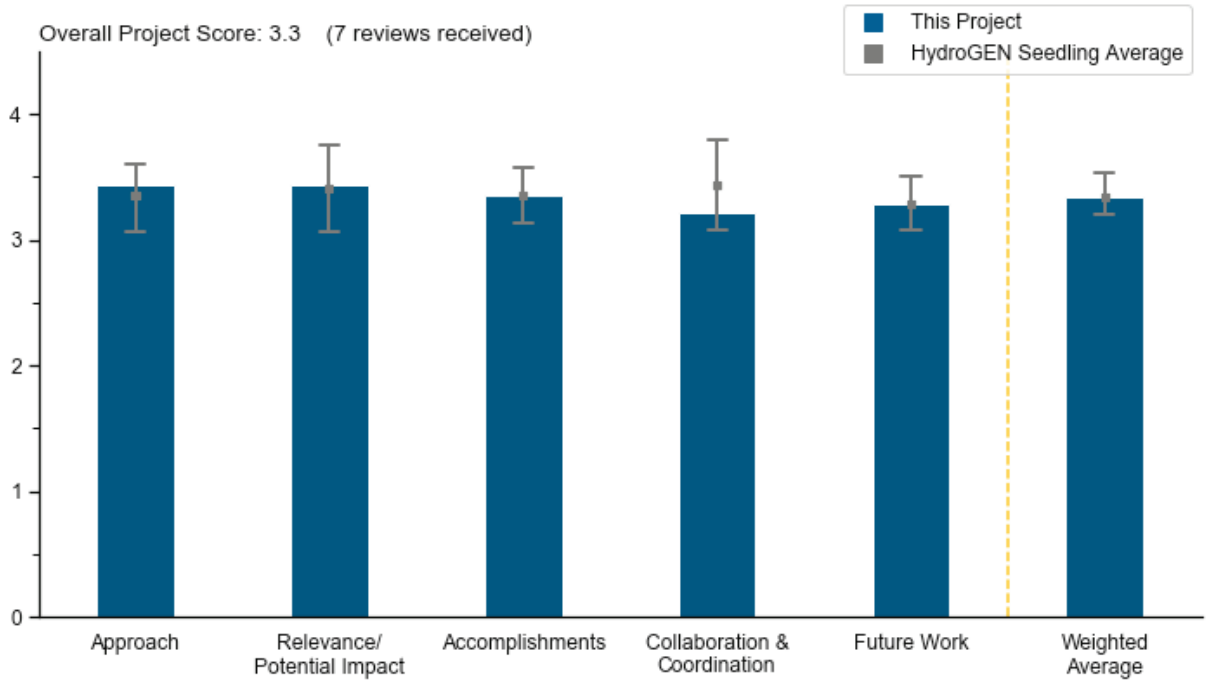
Project #P-176: Development of Durable Materials for Cost-Effective Advanced Water Splitting Utilizing All-Ceramic Solid Oxide Electrolyzer Stack Technology

John Pietras, Saint-Gobain

Brief Summary of Project

This project will develop a high-temperature electrolysis technology that combines a new anode material with a novel all-ceramic stack design. A major innovation and key to the project's effort is the identification and development of nickelate-based materials for the anode in solid oxide electrolysis cells (SOECs). A fundamental understanding of performance degradation and electrode delamination in nickelate-based SOEC materials and interfaces will be developed. Compositions addressing this degradation will be developed to meet specific performance targets: area-specific resistance ≤0.30 ohm-cm^2, current density >1A/cm2 at 1.4 V, stack electrical efficiency >95% lower heating value (LHV) H_2, and stack lifetime ≥7 years. Specific objectives are to optimize the materials and to demonstrate their capability in all-ceramic SOEC cells and stacks by modeling, fabrication, and testing. Results will be validated, and technoeconomic impact will be established.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by HydroGEN Seedling projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying barriers and addressing them through project innovation, as well as for project design, feasibility, and integration with the HydroGEN Consortium network.

- Leveraging a previously developed all-ceramic stack is a viable and cost-effective approach.
- The project follows a solid approach with a promising technology.
- The approaches are appropriate and logical.
- Improving the durability of SOECs is definitely on the critical path to commercial relevance. The team has made a sound hypothesis on how to solve oxygen evolution reaction electrode delamination through chemical composition. There is, however, a lack of modeling to complement (and hopefully expedite) the experimental approach, especially since the compositional space is large. It is recommended that the team engage with other HydroGEN nodes for help.

- The all-ceramic, co-sintered stack approach has been developed by Saint-Gobain over many years, and the issues related to material incompatibilities and sintering shrinkage mismatches have been addressed. There is much value for this stack design if applied to solid oxide electrolysis because pressurization should be easier to achieve. This project aims to use the same concept with a brand new materials set; this seems a bit daunting. For example, co-sintering a ceria-based air electrode with a zirconia-based electrolyte is likely to result in resistive interfaces.
- The approaches are largely effective, but they could be improved; the project contributes to overcoming some barriers. More work needs to be done to demonstrate that layered perovskite is the solution for addressing the delamination issue of oxygen-based electrolyzers. In addition, such materials are very reactive with electrolyte materials, causing potential degradation problems.
- In general, the approaches are excellent. If clearer approaches for achieving target current density were provided, it would be better.

Question 2: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program goals and the HydroGEN Consortium mission.

- Solid oxide electrolysis is a key component of DOE's emerging portfolio of hydrogen production technologies. Saint-Gobain's stack design has some very good attributes for SOEC applications. If this project is successful, Saint-Gobain will be positioned to complete stack and system development and ultimately produce solid oxide electrolyzer systems. Thus, this project has high relevance and a significant potential impact.
- The focus on stability improvement can directly target DOE goals, which will contribute to the commercialization of high-temperature electrolysis (HTE) technology. The work makes a significant contribution to the HydroGEN consortium.
- HTE is a very good platform for DOE to advance through research and development support. This project would benefit from adding a modeling component.
- The project is relevant to high-temperature water electrolysis.
- The relevance and impact of the project are clear.
- The project aligns well with the DOE Hydrogen and Fuel Cells Program (the Program).
- Significant progress has been made, but there are weaknesses that need to be addressed to improve the rate of progress or improve the clarity of the project's objectives and performance indicators. The project contributes to overcoming some barriers.

Question 3: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and DOE goals, as well as the HydroGEN Consortium mission.

- The project started in fiscal year 2019. Good progress has been made to date on milestones.
- The project goals are on track. Evaluating conditions (such as water concentration) should be stated with the various milestones. Hydrogen cost should be calculated for the proposed technology.
- Most project aspects align with the Program and DOE research, development, and demonstration objectives.
- The project has a solid background and a good start, and it should be able to approach the DOE goals.
- Good progress has been made toward cost targets; the approach is unique.
- The project has made progress toward the project goals.
- The work at Boston University is focused on design of rare earth nickelates as air electrodes for SOEC systems. Compatibility issues between the nickelate and doped-ceria phases of composite air electrodes have been identified and are being addressed. However, ultimately, this ceria-containing air electrode will need to be co-sintered with zirconia; this likely will result in a resistive zirconia-doped ceria phase at the electrolyte–electrode interface. There does not appear to have been any work that was performed (or was reported in the presentation) on whether this issue is being encountered or how it will be addressed if or when it is.

Question 4: Collaboration effectiveness

This project was rated **3.2** for its collaboration and coordination with HydroGEN and other research entities.

- Collaboration seems to be proceeding well, with monthly meetings and extensive conversations and discussions.
- The team has a good collaboration history. The current collaborative task arrangement is perfect.
- Collaborations with Idaho National Laboratory and other partners are fairly well coordinated.
- The interactions between collaborators are reasonable.
- The project has been well coordinated.
- It is too early in the project to assess whether there is effective collaboration, but it seems that the only results presented were those obtained by Boston University.
- The project's engagement with partners and HydroGEN nodes seems light thus far; it is mostly just discussions.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The future plans are generally built on past progress and will contribute to overcoming most of the technical barriers.
- The proposed future work is a logical continuation of the presented effort.
- There are no issues with the proposed future work. The team may want to roughly budget more time for short-stack construction for varied compositions. The short-stack construction will likely be difficult, despite the expertise.
- There is a strong experimental plan. The team is encouraged to have discussions with DOE about how to engage HydroGEN modeling capabilities.
- The proposed work can fulfill the project objective. If the work for avoiding the co-firing challenges for the stack were clearer, it would be better.
- The proposed future work is appropriate; more detailed description of the approaches for future work is recommended.
- The reaction between the ceria-containing air electrode with the zirconia electrolyte during co-sintering could be a major death threat to this project. This needs to be assessed and addressed sooner rather than later.

Project strengths:

- The team identified a critical issue with an important hydrogen production technology platform; the researchers developed a hypothesis to address the issue and an experimental plan to test that hypothesis, and they are making good progress on that plan.
- The project develops a complete ceramic system that eliminates many issues on HTE cells while also working on strategies to prevent electrode delamination.
- The project has a clear path to solve the stability issue. The co-firing technique for achieving a stack is promising.
- The all-ceramic stack design has advantages for SOEC applications.
- The project's main strength is in the approaches to address the identified technical barriers.
- The project has a unique approach and a strong team.
- Some good progress has been made.

Project weaknesses:

- This project has no major weaknesses.
- The initial synthesis and construction of the stack or short stack may take more time than predicted. There are bound to be unforeseen issues with the varied compositions, however small the variation.
- A preliminary cost estimate for hydrogen production using the proposed technology should be calculated earlier in the project.
- There is an absence of modeling to complement the experimental plan. There is relatively minor engagement with HydroGEN capabilities.
- More work needs to be done to demonstrate that layered perovskite is the solution for addressing the delamination issue of oxygen-based electrolyzer. In addition, such materials are very reactive with electrolyte materials, causing potential degradation problems.
- It is highly questionable whether the nickelate or ceria-composite cathode will be compatible with a zirconia-based electrolyte in Saint-Gobain's stack manufacturing process.

Recommendations for additions/deletions to project scope:

- There are no recommendations for additions/deletions to the project scope.
- It is suggested that the team do more durability testing under electrolysis mode. More focus should also be given to the performance demonstrated by the layered oxygen electrode under real operating conditions, on either a symmetrical cell or fuel electrolyzer cell.
- Modeling is suggested to help guide experiments to motivate choices for new electrode compositions.
- The team should evaluate the co-sintering earlier rather than later.

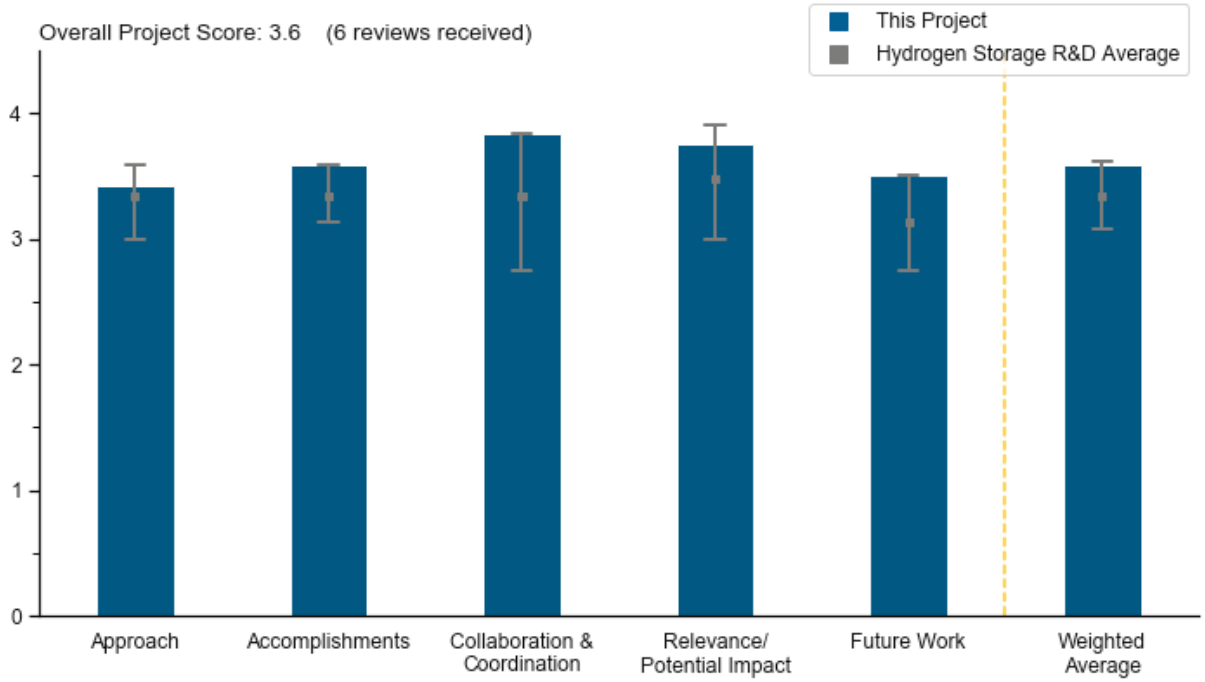
Project #ST-001: System-Level Analysis of Hydrogen Storage Options

Rajesh Ahluwalia, Argonne National Laboratory

Brief Summary of Project

The main objective of this project is to develop and use models to analyze the onboard and off-board performance of physical and materials-based automotive hydrogen storage systems. Specific goals include (1) conducting independent systems analysis for the U.S. Department of Energy (DOE) to gauge the performance of hydrogen storage systems; (2) providing results to materials developers for assessment against system performance targets and goals and for guidance in focusing on areas requiring improvements; (3) providing inputs for independent analysis of onboard system costs; (4) identifying interface issues and opportunities and data needs for technology development; and (5) performing reverse engineering to define material properties needed to meet the system-level targets.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- This project has been ongoing for almost a decade. Its approach is evolving with the needs of the Fuel Cell Technologies Office (FCTO). The project is highly relevant and provides excellent information. Analysis of approaches to hydrogen generation, transport, and storage, both on-site and on-vehicle, is highly informative and fuels discussion.
- This is a comprehensive ongoing project related to onboard and off-board storage of pure hydrogen and liquid hydrogen carriers. The project includes production and conversion of hydrogen (if any). As such, it is an excellent product with a toolset that addresses most hydrogen-related aspects of realistic hydrogen-based energy systems.
- The approach of this project is very strong overall, especially considering the breadth of the project. The project continues to investigate important aspects of hydrogen transport and storage relevant to current

focus areas. There are only a few places where the approach could improve. In the approach for Task 1, 500 tons of geologic hydrogen storage is assumed; however, this storage capacity is available in only a relatively small area of the country. It would be more relevant to include other, more accessible forms of storage in the base case. The approach for Task 3 could be improved by including the packaged volume of the storage cylinders rather than simply including the internal volume.

- The approach is well thought out and relevant to the needs of industry and DOE in understanding the approaches and related cost implications of large-scale hydrogen storage and transportation of hydrogen carriers. It would be beneficial to consider adding an item to the overall cost analysis: the cost of transportation from the cavern storage to the city gate.
- The team involved in this project has a history of adopting excellent analytical approaches with transparent assumptions and logical analyses. The approach toward medium-duty (MD) and heavy-duty (HD) tanks was inappropriate since the internal volumes of compressed natural gas tanks were used to project internal volumes of hydrogen tank capacities, though hydrogen storage tanks would actually be larger in overall size. The MD and HD tanks appeared to be missing the details of the system assumptions, including the additional weight and volume required for the support brackets and container.
- This year, this ongoing project has focused on three aspects of hydrogen storage: bulk hydrogen carriers, geologic storage, and MD and HD storage. The approach is well planned, and the project results are extremely valuable to the hydrogen community. However, with the exception of the MD and HD analysis, it is unclear how the work done contributes to the seven stated critical barriers.

Question 2: Accomplishments and progress

This project was rated **3.6** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- This project continues to make great progress on relevant topics. The comparison of hydrogen carriers is helpful in understanding which materials are suitable and which materials require more scrutiny. With regard to the capital cost of the methanol plants, it would be clearer to include labels on the cost and capacity graph that specify the production method that corresponds to each data point. If the best-case use is autothermal reforming, which is currently not a widespread process, the data could be slightly skewed to favor methanol as a hydrogen carrier. The bulk hydrogen storage study is very well done, and the sensitivity analysis is appreciated. It would be interesting to see how the cryogenic bulk storage system would compare to the analysis presented. The cryo-compressed storage study was similarly well done. It will be interesting to see how the analyses change as data from the Hydrogen Materials Consortium becomes available.
- Methanol is shown to be cost-competitive with compressed gas as a bulk carrier, and salt caverns are shown to be the most economical option for large-scale stationary storage. The project's year-over-year progress is good, and the results are valuable to the hydrogen storage community.
- Accomplishments to date have been detailed and informative. Since the work adjusts to market and industry needs, the progress is quick and accurate. The principal investigator (PI) reaches out to required stakeholders to ensure accurate input into the models.
- The large-scale hydrogen storage and the hydrogen carrier results will be very useful to DOE for planning ongoing programmatic activities. While gaseous hydrogen and methanol appear to be good energy carriers (slide 11), the team should also continue to consider ammonia as an energy carrier. Numerous activities involved in ammonia production may be leveraged to reduce production and overall costs of using an energy carrier. There has been very good progress in bulk hydrogen storage analysis for understanding methodologies and costs.
- The team's accomplishments show great progress toward DOE's goals of understanding large-scale storage costs. It would be beneficial to conduct a comparison of cryo-compression with other storage methods for MD and HD trucks in the future, and it appears that this effort is under way. The advantage of using lower pressure for cryo-compression is the cost reduction that results from using less fiber.
- The inclusion of large production plants for the carriers demonstrates notable progress. The bulk storage analysis is a helpful reference for infrastructure and H2@Scale analysis. The hydrogen storage progress seems to be limited.

Question 3: Collaboration and coordination

This project was rated **3.8** for its engagement with and coordination of project partners and interaction with other entities.

- This project demonstrates an outstanding level of coordination with other organizations. Each project topic has received a great deal of outside support and collaboration.
- Collaborations are numerous and effective.
- This is a very well-coordinated project with a good team of collaborators. Yara North America may be helpful as an additional collaborator on ammonia.
- The project makes use of an excellent set of collaborators. The coordination with participating agencies appears adequate for the purpose of conducting analyses. It would be helpful for the project team to list specific industrial contacts, such as truck manufacturers, involved in data collection.
- The project demonstrates a high level of collaboration with national laboratories and Strategic Analysis, Inc. (SA). However, additional industry support would be beneficial, especially for the carrier analysis.
- There is an excellent team in place to support the project. However, the specific ways in which the team supported the project were not always clear. Though the presenters provided acknowledgements at different points during the presentation, the lack of detail in the acknowledgements did not inspire confidence in the results.

Question 4: Relevance/potential impact

This project was rated **3.8** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This project is very relevant to DOE's current focus. The inclusion of MD and HD vehicles to the scope of interest and the prevalence of H2@Scale and its associated projects further enhance the project's relevance.
- This work is highly relevant, which is unsurprising, as the direction of this ongoing work is changing on an annual basis. The project provides an excellent toolkit and great information to assist in informing and guiding decisions.
- The project is extremely relevant to the hydrogen community. It provides important analysis that is otherwise missing from the materials-focused projects.
- The data and modeling tools in this project have evolved to a point where they can provide clear and reliable results for a broad set of topical areas important to industry and to the FCTO.
- The relevance of the project to the DOE Hydrogen and Fuel Cells Program is high; however, the project focus seems to have changed from "Hydrogen Storage Options" to hydrogen delivery and infrastructure options.
- The project elements are very relevant to current needs and to the impact storage costs of large-scale production can have on the price of hydrogen. The project increases understanding of the costs of various large-scale elements such as piping and installation. Perhaps there are other approaches to cavern storage lining or research areas that could help reduce the costs of the different elements that determine the storage volume. It is unclear whether hydrogen losses from permeation are considered as part of the cost of each storage option.

Question 5: Proposed future work

This project was rated **3.5** for effective and logical planning.

- The inclusion of renewable-specific production, storage, and transport scenarios in future plans is good. This project could benefit from exploring Hydrogen Materials—Advanced Research Consortium (HyMARC)-related hydrogen storage materials and anticipated developments. The use of reverse engineering to determine the desirable materials properties that favor hydrogen carriers would be very interesting, and its success may be likely.
- The proposed work is relevant to the needs and continued improvement of the model. The approach continues to expand the reach of hydrogen storage from the caverns to the city gates. Presumably, the

transportation cost from one location to the next will be included. The MD and HD future work is necessary in helping DOE determine a future focus.

- The future work is appropriate to meet the project goals and milestones. In particular, the proposal to determine the desirable materials properties that favor hydrogen carriers will help guide decisions in other projects for years to come.
- The proposed future work follows logical next steps based on the results of the previous work. The choice to take the analysis to the next level and continue to refine the results is effective.
- The proposed future work includes investigation of important details that will help strengthen the project. However, additional areas of work should be considered for future efforts. It is important to investigate competition related to geologic gas storage, since chemical companies are developing storage in similar manners for ethane and other commodity chemicals. As these potentially feasible geologic gas storage formations are limited in number, storing hydrogen underground might be cost-competitive, compared to other substances.
- In general, the future work is good, but potential improvement from the past analysis is likely to be incremental rather than significant. The future work does not seem to include an attempt to identify significant improvements to the key barriers for hydrogen storage.

Project strengths:

- Thanks to its logical approach, effective collaboration, and good DOE guidance, this continues to be one of the best projects in the Hydrogen Storage subprogram category.
- The project manages to focus on the important aspects of each topic and present them succinctly, a difficult feat for a project of such breadth. It is apparent that a great deal of consideration went into each topic.
- The project team and its capabilities are the project's key strengths. The project's breadth of interrelated topical areas allows it to provide valuable information and data for a realistically large-scale hydrogen-based energy system.
- The project strength is the team, which has an excellent history in hydrogen storage systems analysis and development.
- The project team demonstrates great coordination with all national laboratories and other interested parties. The cost analysis and break-even point comparison of technologies are greatly detailed.
- This excellent project addresses the storage, carriers, and alternative storage approaches on MD and HD vehicles.

Project weaknesses:

- Though it is difficult to find any weakness in the project, an investigation of the electrochemical production of ammonia may be beneficial.
- This is a strong project with very few weaknesses. The only glaring omission is the lack of consideration of liquid carriers for the bulk hydrogen carriers section.
- Overall, there are some aspects of the project that lack clarity. It is understood that a great many assumptions are required to perform analyses such as these; however, more detail should be provided to support reviewers' understanding of project decisions. Most of the project is well described, but there are a few areas, such as the methanol plant capacity chart, which could use a few more details.
- The project title, "Hydrogen Storage Options," is misleading, as the effort has been related mainly to hydrogen delivery carriers and infrastructure bulk storage. Also, the project should attempt to include infrastructure companies and other references to validate project results.
- The project team has not clearly communicated information or feedback from its collaborators. It is clear the PI is communicating with industry, but no industry participants other than BMW are listed.

Recommendations for additions/deletions to project scope:

- There should be a systematic exploration of transport and storage performance and cost of hydrogen and hydrogen carriers from renewable sources. This exploration should cover interstate, regional, and local levels of hydrogen production integrated with renewable resources.

  - It would be interesting to compare glass microspheres to CH_3OH, NH_3, and MCH for long-haul hydrogen transport. Glass microspheres flow like liquid and can be reversible and cycle similarly to MCH/toluene. However, these properties depend on material permeability versus temperature and wall thickness. A performance of 10–20 g/l and 10–14 wt.% can be achieved, according to 1995 data.
  - For CH_3OH, NH_3, and MCH, forecasting analysis needs to consider the anticipated demand growth rate coordinated with fuel cell electric vehicle production rate, rate of availability of geologic hydrogen storage facilities, and H2@Scale-based hydrogen demand growth rate. This translates to the large-scale production/conversion facility installation rate.
  - For normalizing cryo-compressed pressure vessels, the term to consider when describing thermal input rate into the cryogas should be watss per kilogram (or maybe watts per 100 kilograms) of hydrogen stored, rather than simply watts (slide 25).
  - The team should consider collaborating with Yara North America on large-scale anhydrous ammonia production, storage, supply, and transport.
  - At this point in the project, it may be useful to consider adding perturbation analysis of hydrogen transport and storage that incorporates realistic failure or disruption scenario effects on specific hydrogen production-to-end-use configurations.
- The hydrogen carriers should be compared to liquid and cryo-compressed hydrogen to complete the baseline. It would be useful to determine whether cost savings from using a previously excavated site (e.g., a depleted salt mine) for geologic storage are possible. The project's work toward critical barriers is very relevant to the hydrogen community. Project barriers should be updated to include additional barriers that match the work being done, as opposed to altering the project to better meet the barriers.
- The project should return to analyzing hydrogen storage options and opportunities, or at least strike a balance between hydrogen storage and delivery concepts. Since SA has, in the past, conducted the cost analysis for Argonne National Laboratory (ANL), the cost analysis could be deleted from the project scope. This could be an opportunity for ANL to focus on the technical analysis and have SA conduct the cost analysis for carriers and other infrastructure concepts.
- It would be interesting to see how bulk underground hydrogen storage compares economically with other chemicals. Considering the limited number of sites appropriate for bulk storage, it would be interesting to determine whether development for hydrogen storage is economically favorable or whether industry would use these sites for other purposes.
- It would be useful to compare conformable hydrogen storage technology using a volumetric storage density metric. Conformable hydrogen storage is improving and, if permeation issues are resolved, it offers a huge on-vehicle storage advantage volumetrically.
- The project team should include cryo-compressed storage on MD and HD vehicles in cost analyses.

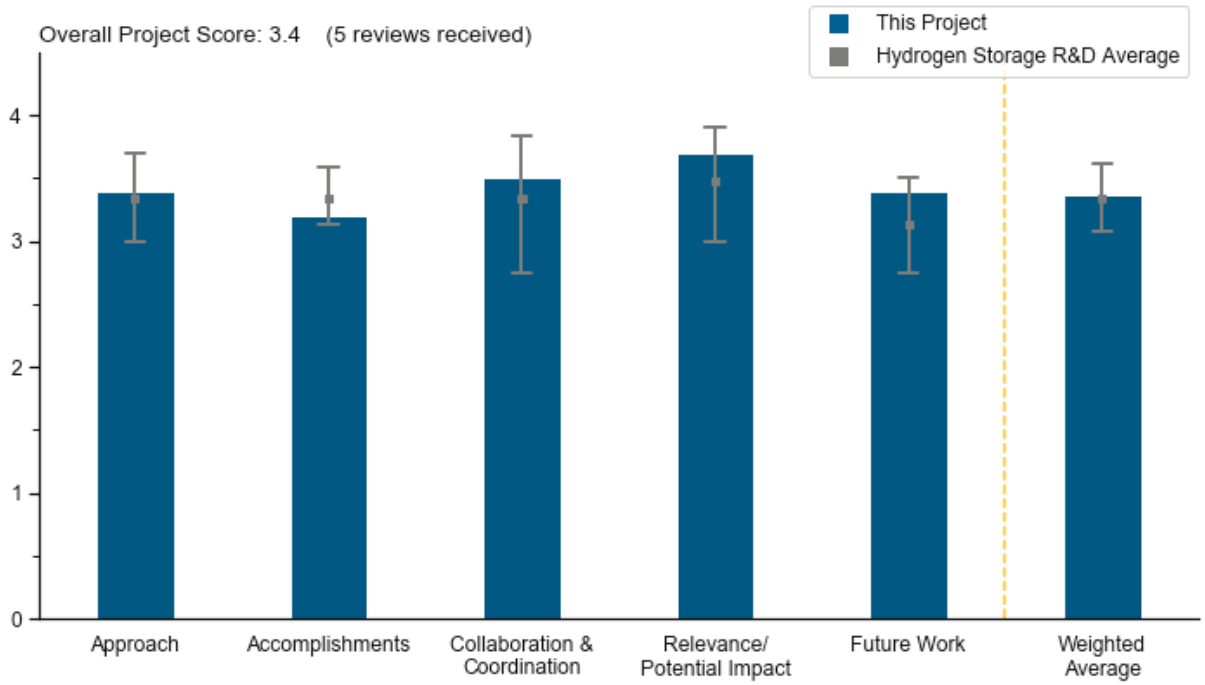
Project #ST-100: Hydrogen Storage Cost Analysis

Brian James, Strategic Analysis, Inc.

Brief Summary of Project

The goals of this project are (1) to conduct independent Design for Manufacture and Assembly (DFMA) cost analysis for multiple onboard hydrogen storage systems and (2) to assess/evaluate cost-reduction strategies to meet the U.S. Department of Energy (DOE) cost targets for onboard hydrogen storage for different types of fuel cell electric vehicles (FCEVs).

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- This project focuses on the cost of hydrogen storage systems, an essential component of fuel cell adoption. This project complements other projects well. This year, the focus has shifted to medium-duty vehicle (MDV) and heavy-duty vehicle (HDV) applications, which matches auto industry trends. Previously calculated values have been updated to reflect changes in carbon fiber price and inflation.
- The approach is sound and addresses project barriers. Updating information and pricing based on new data is essential to staying relevant. Pricing baseline updates prevent the presentation of misleading or outdated information. Comparison of light-duty vehicles (LDVs) with MDVs and HDVs is useful in understanding what learnings can be leveraged and what cost increases can be expected.
- The team involved in this project has a history of adopting an excellent DFMA-based approach with transparent assumptions for economic analysis of hydrogen storage systems. This past year, the approach provided incremental refinements to past analysis and focused only on compressed hydrogen. The approach would benefit from the inclusion of a cost analysis of other projects within the DOE portfolio.
- The approach employs analysis of onboard storage packaging and economy-of-scale pricing for MDV and HDV hydrogen storage. The model updates, which correct for inflation between 2007 and 2016, are

important, although a little late. The general approach enables a clear understanding of storage system cost predictions and shows challenges and alternatives for onboard storage on HDVs.
- The approach is relevant to current areas of investigation and includes the use of a strong industry-developed tool in DFMA.
- This cost analysis could be used to provide recommendations for future research topics and/or targets.

Question 2: Accomplishments and progress

This project was rated **3.2** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The analysis of MDV and HDV sales trends is excellent. The team has made good progress on its LDV hydrogen storage tank comparison. The team provides a detailed analysis of carbon fiber pricing with updated pricing data. The demonstration of the impact updating 2007 costs to 2016 costs is excellent.
- The project has done an excellent job painting a clear picture for HDV storage configuration options. The project also explains the impacts of component choices and economies of scale on hydrogen storage designs. The suggestion (in slide 9) that the models may overestimate costs also suggests that the project team should revisit the models and seek more input from industry.
- This year's incremental progress includes updates to the carbon fiber price and low-volume LDV hydrogen tank system. These updates are useful and important to establishing a new DOE record for an industry reference. Unfortunately, the cost opportunity updates make only a minor change in the 2015 record after the addition of the inflation adjustment. The medium-/heavy-duty (MD/HD) hydrogen storage system background was provided, but the cost information was not provided.
- Good progress has been made on overcoming identified barriers. The cost model and associated adjustment of the dollar basis appear to be well done. Based on the market scoping, MD and HD FCEVs are a potentially strong market for the creation of American manufacturing jobs. The packaging options could have been a little clearer; the chart provided is very difficult to understand without labels. The reason for lumping cab and roof-mounted options together under MDV is unclear. The team should justify this choice and determine whether the aspect ratio differences justify the assumption that they will be the same mass.
- Initial scoping of MD and HD applications and an updated carbon fiber cost in relation to LDVs are presented. The accomplishments appear to be relatively low, compared to previous years.

Question 3: Collaboration and coordination

This project was rated **3.5** for its engagement with and coordination of project partners and interaction with other entities.

- The team engages in excellent collaborations with national laboratories and industry. Furthermore, the team leverages two industry experts for additional credibility.
- The project appears to have an appropriate level of collaboration with national laboratories and industry. It is excellent that the project team connects with carbon fiber and component suppliers to ensure the cost estimates align with current material and component costs. Since the tank is the dominant cost for the hydrogen storage system, additional communication with tank suppliers may be useful for validation of estimates.
- The project coordination appears fairly strong. The project draws on a good mix of industry groups and national laboratories. It would be interesting to see how the data would differ if actual material suppliers, not system manufacturers, were consulted in carbon fiber pricing.
- Collaborations appear to be appropriate and well utilized. For this type of analysis, a more formal collaboration with original equipment manufacturers (OEMs) may be appropriate.
- The project's collaboration team is well equipped and well-coordinated to provide the very useful results in this presentation and to extend the analysis and its applications. However, the project does not seem to collaborate with FCEV OEMs of LDVs, MDVs, and HDVs who can likely provide valuable insight on costs and design options for hydrogen storage systems.

Question 4: Relevance/potential impact

This project was rated **3.7** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This project is highly relevant and provides critical information for the Hydrogen and Fuel Cell Program in the form of a cost assessment that ultimately feeds into DOE strategies for the commercialization and future success of FCEVs. The project sets itself apart from other DOE projects by providing a cost analysis and assisting other projects in the portfolio with cost projections.
- This work is very relevant and high-impact, as the price of carbon fiber is the main cost driver of hydrogen storage systems. The detailed and thorough analysis presented in this project allows for a strong understanding of this key market's needs for development.
- The project provides excellent go-to information necessary for making critical choices in MDV and HDV hydrogen storage system design. The project also provides sensitivity analysis for all FCEV storage systems. This analysis assists DOE target initialization and evolution.
- Without accurate and relevant cost information and predictions, it would be extremely difficult to understand where the market needs to focus to move fuel cells and hydrogen into the competitive market space. This is highly relevant and has a big impact for researchers and potential users.
- The project aligns with the DOE hydrogen goals. Furthermore, this project is unique in the sense that it takes a very in-depth look at hydrogen storage costs. The impact of the results will most likely be limited to other DOE projects and not the industry as a whole, as OEMs tend to conduct cost analyses independently. In other words, the project may have an impact on policy but not on commercialization. However, the project methodology may be adopted by some OEMs.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The proposed future work is very strong. The levelized cost of multiple storage methods provides a great tool for comparison. The analysis is a great tool for guiding the development of the forthcoming targets for MDVs and HDVs. The application of the analysis to H2@Scale will be immensely useful.
- The models are now able to investigate levelized costs in cents per mile on all storage tank designs, an improvement that will be very valuable to the Fuel Cell Technologies Office (FCTO) and industry. Hopefully, the inclusion of cryo-compressed hydrogen (CcH_2) storage in that process implies that the team will overcome the industry shortcoming of sparse data on the component costs for CcH_2 vessels.
- Informing DOE truck targets and levelizing costs are excellent next steps.
- The proposed work is a logical next step, based on the results presented, and may contribute to overcoming some of the project barriers.
- The future work outlined for this project seems appropriate. However, the scope of future work should include development of novel concepts or the analysis of related concepts in the DOE portfolio to reduce the cost of hydrogen storage systems. The reverse cost estimation could be very useful in the development of material storage or carbon fiber targets.

Project strengths:

- The project's core strength is its team, which has an excellent history in analyzing and developing hydrogen storage system cost estimates. The connection with key researchers and other technology teams (e.g., fuel cell cost analysis) to provide a comprehensive analysis is another project strength. The project team has the cost estimation skills and technical capability to evaluate novel hydrogen storage concepts.
- The project has built up extensive modeling capabilities and an excellent team over the years. As a result, the team can quickly and effectively help FCTO and industry understand cost impacts and configuration options for hydrogen storage systems.
- The project demonstrates detailed analysis and thorough data reporting. The project team successfully coordinates with industry connections.

- The project has a strong methodology that provides a very close estimate of actual prices. The inflation adjustment was well done and will hopefully continue to provide valuable results as the project continues.
- Strategic Analysis, Inc., has much experience with cost modeling hydrogen storage systems, and the list of collaborators is strong.

Project weaknesses:

- The weakness for the project was the incremental progress for this year. The tools and skill set of this project team should be stretched to consider additional opportunities for cost reductions and/or assessments of commercialization potential for other projects in the DOE portfolio.
- As with any cost project, the estimates are only as good as the assumptions. The cost projections for LDVs (slide 15) may be too low because, presumably, only a one-tank system is considered. In the market today, there are no one-tank systems for LDVs.
- The project lacks collaboration with FCEV OEMs. Aside from limitations resulting from lack of available data, it is unclear why CcH_2 storage was not considered in the packaging and mounting design options for HDV applications, given the known smaller dimensions that affect the volumetric requirement. Since carbon fiber is the dominant cost factor, it would be worth knowing the CcH_2 total baseline cost for carbon and its incremental reduction.
- The project could provide more clarity overall. Some of the charts are unclear, and descriptions of the work should be more detailed. The model should focus on smaller-scale production, as that is the more near-term case.

Recommendations for additions/deletions to project scope:

- The project team should develop a list of opportunities for DOE and researchers to consider for further reduction in hydrogen tank system costs. The project team could also determine the material cost target by conducting a reverse cost estimation of various material-based systems. In addition, the project team should consider determining the potential cost savings for other project efforts in the DOE portfolio.
- Two- and three-tank systems should be considered for the 700 bar Type IV systems, taking into account the stored hydrogen and balance-of-plant (BOP) configurations of the three commercial LDVs today (Toyota, Honda, and Hyundai). A one-tank system does not seem practical, considering LDV packaging restrictions. Therefore, the cost estimates may be too optimistic.
- The project should increase collaboration with FCEV OEMs to incorporate the industry perspective on storage system component choices, costs, and general packaging strategies. At this point, metrics such as dollars per kilowatt-hour, kilowatt-hours per liter, and kilowatt-hours per kilogram are not universally useful. These metrics are not very helpful in comparing FCEVs to battery electric vehicles since the BOPs are very different and the actual values for such metrics depend on the fuel cell efficiency in the system. The familiar, and more useful, units of measure should be dollars per kilogram, kilograms of hydrogen per liter, and kilograms of hydrogen per kg system.
- The project should include BOP data, though it appears to be on its way soon.
- No modifications to the project scope are recommended.

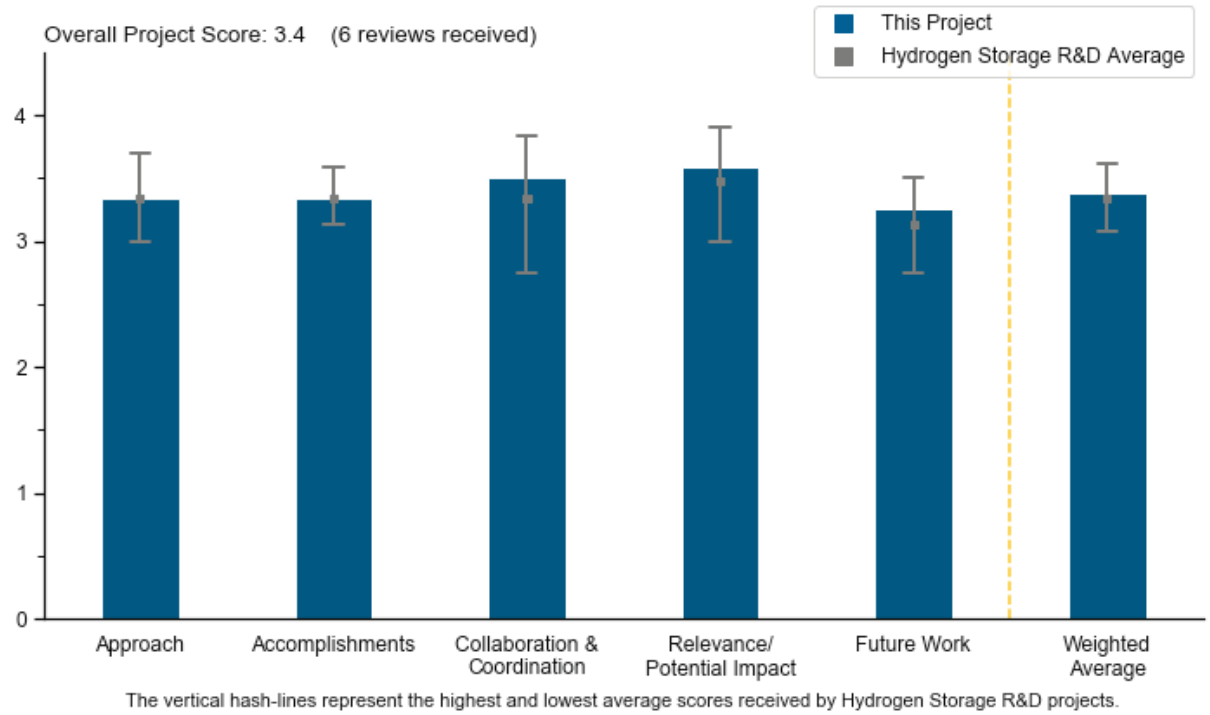
Project #ST-127: Hydrogen Materials–Advanced Research Consortium (HyMARC): A Consortium for Advancing Hydrogen Storage Materials

Mark Allendorf, Sandia National Laboratories, and Tom Gennett, National Renewable Energy Laboratory

Brief Summary of Project

Critical scientific roadblocks must be overcome to accelerate materials discovery for vehicular hydrogen storage. The project objective is to accelerate discovery of breakthrough storage materials by providing capabilities and foundational understanding. Capabilities will include computational models and databases, new characterization tools and methods, and customizable synthetic platforms. Foundational understanding is needed for phenomena governing the thermodynamics and kinetics-limiting development of solid-state hydrogen storage materials.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.3** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach is comprehensive, broadly based, and multi-faceted. It comprises an impressive array of material synthesis, advanced diagnostics and characterization, multiscale theory and modeling, and innovative processing methods to address critical issue barriers that affect our fundamental understanding of hydrogen sorption processes and reactions in hydrogen storage materials. The approach adopted in the Phase II efforts builds directly upon the foundation established in Phase I, and it is well focused on the critical issues that limit the performance in candidate storage media. The consolidation of the HyMARC and Hydrogen Characterization and Optimization Research Efforts (HySCORE) consortia has facilitated the development of a more coherent and rational approach that avoids unnecessary duplication and overlap. The consortium is also provided with excellent technical collaboration and support for related "seedling" projects, thereby augmenting and extending the ability of those projects to achieve their technical goals.

The scope of the overall approach has been extended even further in this reporting period by the incorporation of a new technical effort on hydrogen carrier materials.

- Using a multipronged attack is meritorious, and lines of research and engineering are addressed at barriers; though many or most projects are at the front end of the development process, so it may not be clear to outsiders where the connection is to those barriers, but the connection is there. The adsorbents, absorbents, and hydrides are more or less the mainstream and of course must be included. Carriers are a nice addition to the approach both for their potential use in vehicles and, more likely, for moving hydrogen (for example, as highlighted in the plenary talks). The overall project portfolio is well designed, as can be seen by the many barriers addressed and the quality of the individual projects for attacking those barriers. Most of the projects are feasible; a few are high-risk but also high-reward, and a portion of that kind of work is good management.
- The Annual Merit Review (AMR) project presentation clearly aligned the focus area objectives with the U.S. Department of Energy (DOE) hydrogen storage system targets. The matrix of focus area tasks versus DOE targets was very effective in communicating the approach and responsible teams. A suggestion would be for the project team to attempt to quantify the system-level improvements if the focus areas are successful. This sensitivity assessment could help in prioritizing the many identified focus areas. For example, in the past, Jeff Long provided estimates of possible storage density improvement with several hydrogen molecules binding to a single open metal site. The Phase II approach and structure appear to be better than those of Phase I since the tasks are aligned to specific material storage technologies with supporting focus areas.
- The Phase II extension has brought storage on board for four additional years. HyMARC is covering the vast space in modeling and characterization at multi-length scales. High-risk–high-reward opportunities are core parts of the task. It was nice to see that tasks were added for seedling support and for the Data Hub. Separating advanced characterization into a new task is also a very good strategy. Having focus areas for the sorbent and metal hydride materials makes a lot of sense and is a wonderful management tool. The focus areas are mapped onto DOE targets and also mapped with the multi-laboratory teams focused on the topic. This should continue for the new and/or future focus areas. Face-to-face meetings twice per year with some focus on the seedlings is a great plan for keeping tasks organized. The structure of focus areas specifically for advanced characterization (and perhaps for computational materials) should be made clearer. On the one hand, these serve to develop new tools and computational approaches. On the other hand, these are tools expected to undergo utilization by other (e.g., sorbent and metal hydride) focus areas. It would be wonderful to separate the topics and tasks related to tool development from those related to tool utilization by other (e.g., sorbent and metal hydride) focus areas. This would provide a clearer, better-defined understanding of the importance and role for each of these.
- The high-level overview approach that was presented is along the same vector as last year and builds on the Phase I work. A new addition is the hydrogen carrier work related to the H2@Scale activity. The individual projects under HyMARC that are working on the new hydrogen carrier work are at present focused on new concepts and materials for bulk storage and transport. The high-level overview of the HyMARC approach to the carrier work includes developing metrics and targets via a technoeconomic analysis. A recommendation would be that, before the individual projects go down the research and development (R&D) path too far on developing new concepts and materials, HyMARC leadership should move quickly and with urgency to develop the technoeconomic analysis model(s), such that HyMARC leadership can ensure that the ongoing R&D efforts have the greatest potential for success and the current R&D efforts are not spent on concepts that cannot meet the metrics.
- The new approach in dividing tasks between 1 and 6 is rational. Because Phase II has a shorter duration of operation, it is unclear if the approach will produce the desired results. It is a good start for Phase II.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Solid progress was made in all core R&D areas. An impressive publication record based on Phase I work is evident. Especially impactful results were obtained in Phase I on the importance of the following elements:

  - Hydride surface chemistry on sorption reactions; joint theory and experimental work on hydrogenation and dehydrogenation reactions in $Mg(BH_4)$ and Li_3N, including $Mg(BH_4)_2$ phase diagram determination and reduction of activation energy by nanoscaling and additive incorporation
  - The application of sophisticated in situ or in operando diagnostic tools to explore material and surface properties at relevant pressure and temperature regimes.

  Likewise, important foundational work was conducted on improving binding energy and storage capacities in metal–organic frameworks (MOFs). The technical effort on hydrogen carriers is just under way. A well-formulated plan has been developed to employ HyMARC expertise to make progress in this important technical area. A general comment is that a more keenly focused effort on the critical problem of slow hydrogen sorption kinetics in metal hydrides is needed. This will require the formulation of a more coherent and coordinated strategy.
- The project has clear goals and is making progress toward them. The project's previous work has been extensive and has made a number of advances in understanding fundamentals, developing new, important techniques, and building up and using the theoretical underpinnings. The proof of two hydrogen per center is a big step forward (though there is still much to do to make it commercially viable). This is likewise for the development of a 21 kJ MOF. The reduction of the $Mg(BH4)_2$ desorption temperature is also a move forward. The advances in measurement via high-temperature and high-pressure pressure–composition isotherm (PCT) and high-pressure and high-temperature thermal property measurement are both excellent for understanding the scientific and engineering applications of the materials being developed. The project team is meeting milestones. It would have been preferable to see more actual numeric progress against goals for this big a project (in reference to Phase I), but these things take time.
- The AMR project presentation provided an excellent summary of the Phase I accomplishments that "moved the bar" toward DOE targets. The HyMARC team also had an impressive number of publications and patents. The progress seemed to be appropriate for the Phase I effort. The items that "moved the bar" were clear, but the quantification of how much the storage system bar moved was uncertain. The HyMARC team should attempt to evaluate progress based on system-level improvements or potential enhancement to the system, since a certain material-level enhancement may not have a significant impact on the system.
- Much of the discussion on accomplishments was directed toward what HyMARC accomplished in Phase I, and most of that was covered in the 2018 AMR presentation. There was little discernable high-level discussion of what HyMARC has accomplished since entering Phase II. From the individual project presentations, plenty of progress has been made in Phase II; it would be useful to have seen a cogent summary of highlights of collective progress, as has been done in the past, and less of a discussion of Phase I progress. To assess progress of HyMARC's foundational research aimed at filling in the "knowledge gaps" to enable R&D to accelerate the discovery of new materials or modifications of existing ones, it would be useful to have a clear and measurable graphical summary slide that addresses how HyMARC work is "moving the needle." For example, in the work on understanding how to address the kinetics barriers of hydrogen release or reuptake, it would be very helpful to present a plot of how HyMARC's various approaches (nanoscaling, nanoconfinement, etc.) have resulted in rate enhancements. It should not be difficult to extract maximum and average rates of hydrogen release from the instances in which HyMARC research has shown gains, and compare these improvements in kinetics against the onboard hydrogen-release-rate target. John Vajo has done some of this tabulation for the systems that interest him, and it is very useful and illuminating as a measure of how effective the "electrolyte" approach can be, relative to the target. This should be done for other areas as well, such as HyMARC's approach to understanding how to alter thermodynamics of release or rehydrogenation, and how the resulting work has enhanced the thermodynamics with respect to the idealized thermodynamics "window" for onboard storage and regeneration. These sorts of summaries would help greatly in the translation of HyMARC's foundational research approach into demonstrable progress. HyMARC has done a nice job of working with the seedlings to help them gain access to various HyMARC capabilities, accelerating their progress. Clearly HyMARC leadership has developed this culture of assistance among the individual HyMARC projects, and it is applauded.
- The group is making progress and has many publications to show for it. In the reviewer-only slides, it would have been nice to see a list of publications.
- The project has not had enough time to produce significant progress. The tasks and plans are in place. The leads are engaged with the team members.

Question 3: Collaboration and coordination

This project was rated **3.5** for its engagement with and coordination of project partners and interaction with other entities.

- Extensive collaborations are vital elements of the consortium. The reviewer strongly supports the consolidation of the HyMARC and HySCORE activities. The effective management of such a large and multifaceted effort can be challenging, especially with regard to avoiding unnecessary duplication and overlap of technical activities. Although that clearly remains an issue, the principal investigators (PIs) are making good progress to ensure that focus areas are clearly established, well-developed lines of communication among the different groups are in place, and technical synergies are exploited. A serious challenge will be the acknowledgement of when projects and tasks should be brought to an end, allowing resources to be focused on more fruitful pathways. Excellent support of seedling activities is evident; collaborations with the HyMARC core team have effectively reinforced the seedling efforts.
- The extent of collaborations and coordination continues at the high level set during prior years. Internal collaborations and coordination among the HyMARC partners appear to remain strong, and collaborations with the DOE Office of Basic Energy Sciences facilities at Lawrence Berkeley National Laboratory's Advanced Light Source facility appear to be working reasonably well. Collaborations with the seedlings appear to be solid, as judged by the seedling presentations and the individual HyMARC partner presentations. Overall, the level of collaboration is commensurate with the scale and scope of the individual projects and is commendable. With the new activity in hydrogen carriers, HyMARC leadership needs to get out in front of the R&D activities with a well-developed set of metrics to coordinate these efforts to provide the largest impact.
- The project is pretty much an inherently high-collaboration program, but it also pulls in many outside groups. The use of seedlings and the support they get speaks to the coordination. The team seems to have a good approach for coordinating work, as well as spreading advancements and understanding through the many groups in the team.
- The project has a significant level of collaboration among the national laboratories. The presentation slides showed well-coordinated roles and responsibilities for the various national laboratory teams. A possible improvement to the collaboration is the consideration of industry or other resources to ensure the approaches being recommended have the potential for commercialization in the future.
- The HyMARC program integrates multiple institutions. The support for four seedlings is also a good addition to the portfolio.
- The Phase II seedlings include the University of Michigan, Liox Power, Inc., and the University of Hawaii. It seems like collaborative partners are chosen based on their past familiarity with the PIs. The project team has missed opportunities in the form of a more level playing field, the inclusion of a broader community and underrepresented groups, an open approach to seeking seedlings, and decision-making based on the potential for increasing the broader impact of HyMARC and establishing future U.S. leadership. This can be improved.

Question 4: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- HyMARC remains the centerpiece of DOE's hydrogen storage program and is expanding its work into hydrogen carriers in support of the H2@Scale initiative. Despite years of excellent work across decades of R&D worldwide, including significant DOE-funded efforts in the United States, no single material has yet to be able to fulfill the stringent requirements for onboard vehicular storage. HyMARC's approach to this problem is to take a step back and fill in the knowledge gaps that address critical barriers to success. Among those the consortium is addressing are understanding how solid-state complex metal hydrides develop into complicated multiphasic materials as hydrogen release proceeds. Gaining an understanding as to how the various interphases affect mass transport, the diffusion of reacting species, etc., and how these features influence reaction pathways and kinetics is critical to being able to ascertain whether there are routes to modification of materials or entirely new materials that can overcome these key barriers that have

confounded prior hydrogen storage researchers. It is a hard—very hard—problem HyMARC is addressing, and the team is making progress. HyMARC has brought most of the right tools and capabilities, human and otherwise, to bear on the problem. The approach is potent: integration of experiments with computational modeling, coupled with state-of-the-art characterization capabilities, while maintaining a focus on the key barriers. This approach provides great potential to make a significant impact on the search for solutions to this vexing materials problem that has such a significant potential upside for cost-effective onboard storage.

- The HyMARC consortium is the centerpiece of the DOE Office of Energy Efficiency and Renewable Energy hydrogen storage activity, and as such, it is a critical element of the DOE Hydrogen and Fuel Cells Program (the Program). DOE's decision to create this consortium is sensible and commendable. Moreover, the consolidation of the HyMARC and HySCORE activities has resulted in reduced confusion, duplication, and complexity. The consortium is providing a foundation for understanding the complex processes operative during hydrogen sorption reactions in solid-state and liquid media. That understanding is crucial to guiding the development of improved materials that can meet DOE storage targets. The consortium provides a much-needed framework for making rational decisions concerning new materials development.
- The project has relevance for the Program in the area of materials-based hydrogen storage, although the impact is difficult to quantify since the ultimate influence on system-level attributes is uncertain. The project should consider using this highly capable team to evaluate the storage system benefits if this research is successful.
- A major, coordinated effort is the only way that a solution other than compressed gas is likely to be found. The addition of "seedling" studies and higher-risk, low-investment options is a good adjunct to the main-line, longer-term approaches. The emphasis on fundamental understanding is key, as the past decade has probably exhausted the options based on current understanding. Using theory to help guide experiments and using experiments to ground theory is obviously an excellent approach.
- The project supports the broad task related to sorbent and hydride materials. The most relevant problems have been identified. Without an effort as large and coordinated as the HyMARC program, progress on these topics would be substantially slower.
- Phase II is new, and the available data is not ready for answering this question or providing suggestions for improvements.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The future work includes the development of a data hub, machine learning, and the expansion of hydrogen carriers as a focus area. These are all very good directions for the portfolio to move. The team should continue to develop areas with DOE targets in mind and also provide a clear picture of which groups will work on each task under these new areas.
- The future work on hydrides and sorbents builds directly upon the work conducted in Phase I. Plans are also in place for exploring new and novel hydrogen carrier approaches. With the introduction of new reaction chambers, the impact of the in situ and in operando diagnostics could be significant. Continued efforts are proposed to create a robust and streamlined management structure capable of effectively coordinating the large number of consortium activities. This will be essential to ensure that the R&D priorities are established and implemented in the most objective and rational way. There is a need for a well-formulated strategy keenly focused on significantly improving hydrogen sorption rates in complex metal hydrides.
- The future work for this project associated with Phase II has the right direction for improving the understanding of materials-based hydrogen storage. The concerns for future work are that the list of focus areas is extensive and the prioritization of these tasks is not understood.
- Each area and management has an appropriate set of goals for the year.
- The proposed future work description was adequate but somewhat uninspiring, given the urgency to fill the knowledge gaps. As this is an overview presentation, a roll-up of the highlights of the individual HyMARC project plans would have helped to place the ensuing individual presentations in context of the bigger picture. The future plan includes an evaluation of progress toward the "applied" focus areas, presuming that to mean quantifying the HyMARC-derived improvements in thermodynamics, kinetics, etc. This is a topic that should be addressed and updated in each AMR. Otherwise, it is difficult for the community to gauge

the progress being made in a quantitative manner. The future work in the hydrogen carriers area is to determine the state of the art. Ideally, this would have occurred prior to starting the experimental work that is already ongoing. Factoring in the much-needed technoeconomic analysis of carriers, along with an analysis of the state of the art, will provide a firm foundation for the selection of promising approaches.

Project strengths:

- This is a comprehensive and well-organized technical effort designed to provide DOE with foundational understanding concerning the kinetics and thermodynamics of hydrogen sorption reactions in existing and emerging hydrogen storage materials. The consortium team has expertise in all areas relevant to achieving R&D objectives, including multiscale theory and modeling, novel synthetic methods, and sophisticated material diagnostics. The consolidation of the HyMARC and HySCORE efforts has broadened the scope of the effort and has provided a more streamlined and manageable way to address R&D imperatives with limited overlap and duplication. The addition of the new hydrogen carrier effort addresses an important DOE need and will undoubtedly emerge as a critical element of the overall technical effort.
- The team that has been put together in general has a strength of capabilities and experience. They have developed or are developing access to new and state-of-the-art characterization tools and techniques, including in situ techniques, either through collaborations with appropriate DOE user facilities or through acquisition. A challenge for managing such a consortium is to keep a tight focus on the project's key problems, with a willingness to make changes as required. HyMARC leadership is doing an admirable job of this.
- The project's overall strength is the team's recognition of strengths and weaknesses revealed by the Phase I effort. Repeating such a path will not deliver results. The new definition of tasks is a good starting point to focus on areas of success and try to develop momentum for year 2. At this point, the team is making an effort by thinking through the issues and changing some of the previous issues with coordination that led to inefficiencies that are now getting addressed. It is a promising start by a very accomplished team.
- The strength of this project is the highly capable national laboratory researchers who have extensive history in developing and analyzing hydrogen storage materials. The project team appears to have made notable progress with Phase I and has constructed a good structure and focus for Phase II.
- The strength of the project is in the skill set assembled by the team members. The ability to pursue sorbents, hydrides, and hydrogen carriers with the most advanced computational and experimental tools is impressive.
- The project's strengths include its scale, facilities, people, and seedlings in addition to the main-line program. There are multiple ways to "win," such as in vehicles, transportation, stationary applications, etc.

Project weaknesses:

- The team leaders had to develop organizational structures and organizational tools to make effective progress out of the multidimensional task list. The leaders are well under way to doing this. Several suggestions have been made on the computational and advanced characterization focus areas (namely, that tasks related to tool development be separately and explicitly considered relative to tasks related to tool utilization). These, along with other fine tunings to the overall organization and management structure, will help. However, by and large, the vision and leadership shows through the structures developed as of now.
- There are two weaknesses that are more about the caution needed to manage the current effort to deliver the impact for DOE's investment in this team.
    - The first project weakness is in some of the assumptions about the future of hydrogen storage and the lack of connection to the marketplace. It seems highly internally focused and not connected to the marketplace where any commercial success in this domain will require a good deal of help from HyMARC. One example of internal focus is a turn toward effort in H2@Scale. An effort on sorbents is definitely important, but it is also reflective of the shifts in the Fuel Cells Technologies Office. Since separate funding opportunity announcements on H2@Scale and proposals will be getting reviewed, this can be viewed as an effort by the team to divert resources away from some of the strength of HyMARC in Phase I and anticipate potential areas where funded research can grow. It is understood that this is a strategic decision that will help the team. It is sincerely hoped that they will use the resources to help the community. Also, in coming years, the project needs to

be justified by demonstrating strong connections to the new efforts starting because of H2@Scale activities and their ability to leverage HyMARC to show a return on investment.

  - The project's second weakness has to do with the lack of spread of leadership to a broader number of people. The verticals are well defined, but the team had the chance to engage new task leads in Phase II and share the load of managing multidisciplinary teams while supporting a more inclusive organization structure for HyMARC. There is tremendous talent in the team, and spreading the load by adding co-leads to the team with different backgrounds, perspectives, and institutional affiliations for different tasks will be highly desirable. This will increase ownership for success to a broader group and train new leaders for the future endeavors. Another approach might be to define leads for cross-cuts. In some sense, theory and computation, data hub (as seen in task six), and characterization are actually cross-cuts and touch all other tasks. Under the current structure, it is hard to find the second and third level of leads for managing the connections between teams with the same degree of quality assurance and coordination. The PIs are encouraged to think more about potential ways of strengthening the matrix in which the current tasks exist and reflect on improving the flow of information, quality, knowledge management, and tracking of progress to build a "dynamic and agile" team, as proposed by the PIs.

- Sluggish sorption kinetics remains the dominant problem in the hydride systems. A stronger emphasis on this important issue is needed. A well-formulated strategy or pathway should be developed to address this important problem. It is hoped that by the 2020 AMR, a definitive statement concerning the principal "bottleneck" that limits sorption kinetics in borohydrides can be articulated. Actual data are needed; it is not sufficient simply to state (as seen on slides 23 and 24) that "[systems with] … reasonable kinetics" will be demonstrated. It is readily apparent that improved access to nuclear magnetic resonance (NMR) capabilities is needed. The importance of NMR as a diagnostic tool for this research cannot be overstated. Although impressive NMR capabilities exist at participating HyMARC organizations, the access to those capabilities seems to be limited. If those restrictions cannot be removed or reduced, then other sources for NMR work should be explored. The use of nanostructures and nanoscale engineering for enhancing hydrogen sorption reactions are important R&D topics in HyMARC and are being addressed by numerous organizations in the consortium. These organizations include, for example, Sandia National Laboratories (borohydride activation reduction, nanointerface engineering, nanoscale defects in sorbents); National Renewable Energy Laboratory (atomic layer deposition on nanoparticles, nanoscaling to improve magnesium hydride thermodynamics and kinetics, plasmonic nanostructures); Lawrence Berkeley National Laboratory (nanocomposites, nanoencapsulation, functionalized nanoribbons); and Lawrence Livermore National Laboratory (theory and multiphase modeling). It is not evident that these numerous yet related activities are being coordinated and managed in a way that ensures proper collaboration and unwanted duplication.
- After several years of pursuing development of the foundational research concepts to address the key knowledge gaps that are barriers to practical materials development for the applications at hand, the HyMARC management should be able to better communicate, in a quantitative way, the extent to which this general approach is having an impact. A potential weakness lies in the H2@Scale hydrogen carrier work that is moving forward without the benefit of metrics to provide rationale for system selection. A potential weakness is in the hydrogen carrier work and prompts a question for the HyMARC leadership team of whether HyMARC has the right set of capabilities and staff with catalysis and/or electrochemical expertise to effectively drive such a program forward with all the organizations involved.
- The project's weakness is that, although the fundamental research is interesting, there is no evidence that the Phase I results have produced any improvements in the storage system attributes. Another weakness is that the project does not include any prioritization of focus areas, and the research seems to be driven more by the preference of the researchers than the impact of improving hydrogen storage system attributes.
- While not a manifest weakness now, there is the potential for the current coordination to fray if it is not actively managed. Also, while the focus on fundamentals is needed, it is possible to lose sight of the eventual goal of application; again, this is not a problem now, but the project leads must be vigilant to always ask, if things go reasonably well, whether this can add value to the hydrogen economy.

Recommendations for additions/deletions to project scope:

- The project team should attempt to conduct simulations of their research on the potential impact to the hydrogen storage system. The HyMARC team should consider using technoeconomic analysis and factors with their hydrogen storage research direction, similar to their planned work with the carriers. The project has several activities still investigating $Mg(BH4)_2$, although this material has been studied for a significant amount of time without a clear understanding of the rate limitation. Therefore, the project team may need to consider another representative material for their fundamental research investigation. Additional information about the HyMARC team involvement with the seedling projects may be useful in future reviews.
- A potential addition to the HyMARC management plan, if it is not already in hand, would be a risk mitigation plan for actions that may be out of the hands of HyMARC. Specifically, it is unclear what the impact would be on the R&D plan moving forward if access to ALS or the Spallation Neutron Source falls through or is significantly delayed—or whether there is a "plan B.'"
- There must be increased emphasis on understanding barriers to sorption kinetics in complex metal hydrides; actual rates must be established. There must also be improved access to NMR capabilities and improved coordination of multiple R&D activities devoted to nanostructures and nanoscale engineering.
- The project team should maintain scope and possibly consider a slight shift of funds to increase the theory group size (with quality postdocs, not new PIs), as that group seems to serve all and may be overworked—or at least might be very able to increase overall program progress quickly with a bit more funding.
- The project's tasks are new and need sufficient time before such recommendations are warranted.

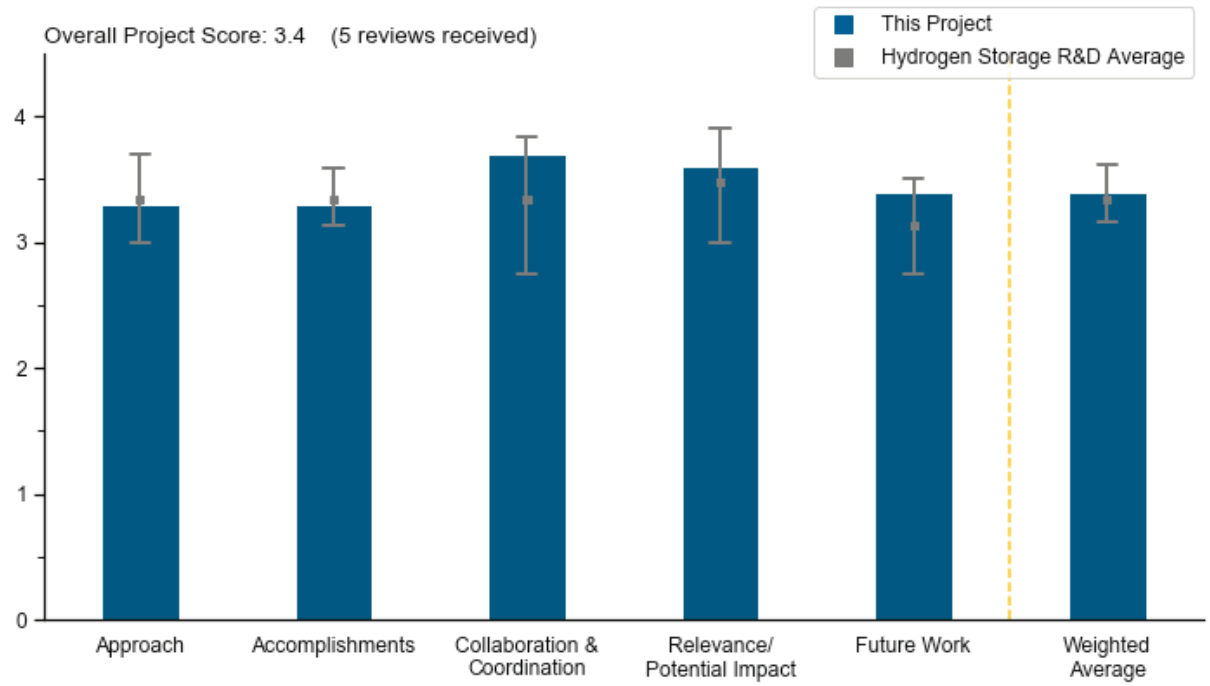
Project #ST-128: Hydrogen Materials–Advanced Research Consortium (HyMARC): Sandia National Laboratories Technical Activities

Mark Allendorf, Sandia National Laboratories

Brief Summary of Project

This project addresses a lack of knowledge about hydrogen physisorption and chemisorption. Researchers will develop foundational understanding of phenomena governing the thermodynamics and kinetics of hydrogen release and uptake in all classes of hydrogen storage materials. Sandia National Laboratories (SNL) will (1) provide data required to develop and validate thermodynamic models of sorbents and metal hydrides, (2) identify the structure, composition, and reactivity of gas–surface and solid–solid hydride surfaces contributing to rate-limiting desorption and uptake, (3) synthesize metal hydrides and sorbents in a variety of formats and develop in situ techniques for their characterization, and (4) apply multiscale codes to discover new materials and new mechanisms of storing hydrogen.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.3** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach adopted by the SNL HyMARC team is systematic, rational, and well formulated. A robust combination of theoretical, modeling, and experimental work is being employed to address issues that are critical to our understanding of phase energetics and kinetics of hydrogen sorption reactions in complex hydrides and sorbent systems. However, a keener focus on understanding the rate-limiting step(s) in dehydrogenation and hydrogenation of metal borohydrides is needed. Extensive collaborations are in place and are reinforcing and expanding the scope and depth of the SNL-led effort. The SNL team is also providing valuable support to associated seedling activities.
- The Phase II effort divides the tasks into three areas: sorbents, metal hydrides, and hydrogen carriers. The project has a good balance between theory and experiments. Density functional theory (DFT), DFT-derived

potentials for molecular dynamics, and calculations of thermodynamics have progressed well. It is not clear how much kinetics work started in Phase I; the multiscale approach presented will be pursued in Phase II.

- The SNL technical effort has provided many outcomes related to sorbent materials and metal hydrides. One area in which this group has excelled is in the development of new advanced instrumentation for measuring hydrogen on surfaces and with X-ray absorption spectroscopy (XAS).
- The presentation did not explicitly contain an overarching "approach" slide, so one must read between the lines a bit.
    - The SNL approach continues to be directed at providing the so-called foundational underpinnings that address the barriers in kinetics, thermodynamics, etc. for complex metal hydrides that are critical to making progress toward the targets. The experimental focus remains on understanding how nanoscaling may affect the kinetics and thermodynamics of complex metal hydrides. Two other areas of investigation appear to be getting some attention: the area of sorbent packing to improve the volumetric capacity of sorbents and a new area of hydrogen carriers to support the H2@Scale program. Overall, the approach appears to span a wide range of rather disconnected efforts for the size of the budget; one must wonder if the team members are spread a bit too thin to maintain this breadth of approaches and still keep their eye on the real barrier to success: kinetics.
    - The SNL team has collaborated to develop new low-energy ion scattering techniques to track the rates of hydrogen transport at surfaces and in the near surface. This appears to be a good approach that will hopefully help validate the computational modeling results that are intended to address the influence of buried interphases on the thermodynamics and kinetics of hydrogen release from magnesium borohydride ($Mg(BH_4)_2$). Another approach the team is working with is to understand how to influence the kinetics of dehydrogenation and rehydrogenation with additives or catalysts. The team uses TiF_3 as the precursor to put Ti onto MgB_2, and of course, there is no surprise that this results in MgF_2 being formed. Thus this approach is a little flawed; the team should rather look at other approaches wherein the Ti is placed on the surface without forming other Mg species that might confound the project studies and the ability to coordinate results with the parallel computational studies being performed at Lawrence Livermore National Laboratory (Woods et al.).
    - In the area of trying to further understand nanoscaling effects, the team has prepared a compound in which $Mg(BH_4)_2$ is complexed to the bipyridine (bipy) functionality of a metal–organic framework (MOF). It was not discussed how continued study of this system relates to the condensed phase studies of bulk or nanoscaled $Mg(BH_4)_2$, so the approach was not well explained. Perhaps what the project might focus on is how this is relevant to what Severa and Jensen et al. are doing with another donor ligand–$Mg(BH_4)_2$ system, THFx–$Mg(BH_4)_2$. Maybe there is some synergy to be gained there.
    - To approach the modeling of multiphasic materials relevant to the dehydrogenation and rehydrogenation in $Mg(BH_4)_2$, the team is using a suite of molecular dynamics and DFT techniques to gain information about the interaction potentials between reactants and intermediates such as the arachno-, nido-, and closo-boranes. This appears to be a good approach that has good potential to lend validation and feedback to the HyMARC theory effort.
    - In a rather disconnected approach from the bulk of their work, the project team is working on improving the volumetric capacity of sorbents by exploring the preparation of MOFs in monolith form via sol–gel techniques. While they are being successful, one must ask whether the system chosen is the "right one." It is unclear why they do not focus their effort on MOF-5 or one of the promising systems that Siegel et al. have identified from their machine-learning project. It is also unclear whether this task is a distraction from their work on the kinetics and thermodynamics of complex metal hydrides.
    - In yet another topic, that of hydrogen carriers, their approach is to explore dehydrogenation of diols as liquid organic hydrogen carriers (LOHCs). No rationale was given as to the choice of the carriers selected for research, nor was there a discussion of what the best catalytic routes might be for dehydrogenation (there are hundreds of papers in the literature on glycerol dehydrogenation alone). And lastly, it is unclear whether this approach has considered the technoeconomic analysis out of Argonne National Laboratory that indicates that two-way LOHCs are at an economic disadvantage relative to one-way systems. Another facet of this approach was to explore eutectics of $Mg(BH_4)_2$ as hydrogen carriers. No rationale for this approach was given, nor a discussion of how this could work in practice.
- The project team is attacking many different aspects of the barriers to many paths to success at a variety of levels. Use of materials techniques as well as theory and engineering to advance the performance of

systems should yield a better overall project. The project is part of a larger effort as well, so the team can easily avail themselves of other techniques and insights.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Solid progress has been made in numerous areas of this broadly based research activity. Notably, the development of an improved understanding of how oxides and hydroxides can influence sorption reaction barriers in $NaAlH_4$ (a Phase I effort) is especially intriguing and could be potentially important for other complex hydride systems; determining whether those effects extend to other systems is strongly recommended. Establishment of a molecular dynamics modeling framework capable of assisting development of hydrogen transport models is an important development. It will be interesting to see if the approach used to predict behavior in model systems (e.g., Pd, MgH_2/Mg) can also be extended to more complex reactants. The combination of experiments and theory to develop a phase diagram for bulk $Mg(BH_4)_2$ will undoubtedly pay dividends for understanding the thermodynamic properties and the evolution of reaction products in this important candidate storage system. It will be especially informative and valuable to understand how the phase diagram changes with decreasing magnesium hydride particle size. Likewise, results on force-field modeling of borohydride species created during hydrogen desorption may affect understanding of the thermodynamic properties and, to a lesser extent, kinetic behavior of hydrogen reactions in boron-based materials. Clearly, an important research direction is to develop a better understanding of how additives and catalysts might affect reaction rates in complex metal hydrides. Initial results are promising, but a more seriously focused and systematic research effort is needed. In addition to the work on metal hydrides, the SNL team has made important advances in understanding how novel nanoengineering methods can be brought to bear to alter sorption reaction rates and, possibly, thermodynamics in metal hydrides and MOFs.
- The project team is making good progress toward deliverables and toward surmounting barriers, too. The project has developed kinetic and phase diagram information on key materials, methods to understand molecular- and atomic-level states and changes in state, and science and engineering models, and the team has applied them. Especially appreciated was the blend of science and engineering looking at the encapsulated LiN system, which had lower fundamental capacity but better system capacity owing to a much-reduced heat-transfer system requirement.
- One of the most significant results of this project has been to examine the role of oxygen at the surface of $NaAlH_4$, to reveal that the Al-O-H phases that form change during desorption, and that this may play a role in the desorption pathway and kinetics. This was done by combining simulations with X-ray photoelectron spectroscopy (XPS) experimental data. This is the type of finding that requires a larger group and concerted effort. The research group has shown that the UiO-67 MOF monolith results in an uptake of high volumes of both CH_4 and hydrogen (relative to the powders). These results point to surface-limiting reactions occurring in the powders and not in the monolith. Another major accomplishment is the work shown on slide 15, which really illustrates the advances in moving toward nanoscale hydrides. Because of thermal management of the host structure, volumetric and gravimetric capacity is higher in the nanoscale Li_3N (even with the presence of the "inactive" host structure). Unlike the UiO-67 MOF monolith, consolidated MgH_2 acts as a diffusion barrier to hydrogen. Therefore, forming a fully dense surface layer of it could be problematic (from a mass transport perspective). The capacity drop is likely due to dense MgH_2 formation in the melted sample. MgH_2 is a very slow hydrogen diffuser (like native oxides, it provides an oxygen diffusion barrier in metals). For this reason, a porous layer would work better than a fully dense layer. It could be melted with additive or with gas elution to give porous nanoconfined $Mg(BH_4)_2$ borohydride.
- The phase diagram effort is commendable. Some differences between the previous year's and this year's presentation were noted for the phase diagram of $Mg(BH_4)_2$, but no explanation was provided on the changes. The same is true for the explanation on the role of the oxide layer in sodium alanate. The explanation changed somewhat between 2018 and 2019 in subtle but noticeable ways. The project's new work on eutectics is promising, although much effort in the past on this topic needs to be considered in order not to repeat the effort made under the DOE Metal Hydride Center of Excellence without a strong justification for repeating such efforts. More details were needed on additives and whether any theoretical effort was used for the choice. Overall, there is a strong effort and some gaps in explanation due to limited

scope of the review. The team should consider a more succinct way to connect the summary and conclusions to the data presented and identify the ones covered in the backup slides.

- Overall, the team is making progress, but on a rather diverse set of tasks. It must be asked whether the project would be more productive focusing a bit. It is also difficult to assess progress on the "foundational" approach, as there is a dearth of quantitative statements as to how far the team has "moved the needle" toward a given target. One instance in which the team has provided quantitative data toward progress is on the nanoscaling of hydrogenated lithium nitride; while positive results were described for nanoscaling, it was not made clear how what they have learned would be predicted to influence other complex metal hydride materials. The team continues to make incremental progress on integrating the modeling and experimental efforts directed at understanding what underlies the apparent kinetics issues associated with the multiphasic nature of the dehydrogenation/rehydrogenation of magnesium borohydride/magnesium boride. Where the project has shown nice progress is in developing the combination of low-energy ion scattering, XPS, and gas phase analysis to track hydrogen transport at and near the surface. It will be of interest to see how the team is able to give validation and feedback to the modeling effort in the future such that more rapid progress can be made toward understanding the kinetics barriers in $Mg(BH_4)_2$. The SNL team has made some progress on exploring eutectics and dehydrogenation of polyols for the H2@Scale effort, the preparation of monolithic MOFs for improving volumetric density of hydrogen sorption in MOFs, and molecularly supported $Mg(BH_4)_2$ on a bipy-functionalized MOF. These efforts lacked a firm rationale, and it seems that, while the team members were making progress here, they would perhaps be better served by focusing on the tasks surrounding the integration of theory and experiment on the $Mg(BH_4)_2$ system.

Question 3: Collaboration and coordination

This project was rated **3.7** for its engagement with and coordination of project partners and interaction with other entities.

- Extensive collaborations with other HyMARC core team members and seedling projects are evident. The availability of the SNL high-pressure hydrogenation and characterization system and the sharing of high-pressure expertise with other consortium researchers have been vital to project success. The consolidation of the HyMARC and HySCORE activities has merged a variety of related projects, and the SNL effort overlaps much of that work. Although it may go without saying, frequent communication and interaction among researchers involved in those related activities is critical and strongly recommended.
- Collaboration is an area where the SNL team excels. They have brought unique SNL capabilities to bear on a number of seedling projects, and their capability in performing high-pressure hydrogen experiments is surely oversubscribed by external collaborators.
- The project has good interaction with four seedling projects that include a number of joint publications. Additionally, international collaborations with Aarhus University have provided a publication on the closo-borates.
- There is extensive, appropriate, and helpful collaboration with a dozen outside groups, many of which are the best in the business. There are clear examples of these collaborations accelerating progress toward goals.
- The list of collaborators is significant. The collaborative effort is opportunistic and not strategic. A better alignment of needs and a leveraging of complementary capabilities in different national and international institutions need to be clearly outlined. Assigning a lead for collaboration and outreach can improve the focus.

Question 4: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- The work accomplished so far points to new directions and suggests that the project will have far-reaching impacts. For example, redefining the role of nanoporous host structures as actively participating in thermal management will open the doors to optimization of new porous materials and hydride combinations that outperform currently studied ones. The study of monolithic MOFs shows that a particular barrier in hydrogen uptake that exists for the powders is ameliorated with compaction. This reframes thinking around the notion that high surface area is necessary for more hydrogen uptake. Such high-density microstructures are not as effective when utilizing metal hydrides (e.g., $Mg(BH_4)_2$, which is melt-infiltrated into graphene aerogels), potentially because the entire monolith could form MgH_2 (which is a slow diffuser of hydrogen). Taken together, these studies point to the ability to tune kinetics by controlling microstructure and open the door to many more possibilities for designing optimal hydrogen storage materials.
- Three major areas are addressed: understanding, materials, and measurement capability improvement. This makes the project highly relevant in theory. The actual work in these areas is all essential to progress in solid-phase hydrogen storage, so this is a highly relevant project.
- The SNL contributions are critical to the success of the HyMARC consortium. The project is well aligned with DOE Hydrogen and Fuel Cells Program goals, and the potential impact of progress toward achieving Office of Energy Efficiency and Renewable Energy goals is significant. SNL's strong support of seedling activities is enabling and accelerating progress on those projects.
- The team has made some very important contributions. The overall talent and innovation were definitely noteworthy in Phase I. In Phase II, although some changes were made for somewhat unknown reasons, the team seems to be making progress toward the goals.
- There is very high relevance and potential impact of SNL and its collaborations in integrating the experimental and modeling efforts in understanding the underlying multiphasic issues of the hydrogenation and dehydrogenation of $Mg(BH_4)_2$. Given that they are also exploring several other rather unrelated areas, perhaps the impact of their efforts would be greater if there were fewer distractions, e.g., fewer tasks outside of the main tasks surrounding understanding bulk and/or nanoscaled $Mg(BH_4)_2$. Perhaps more of an "all hands on deck" focus on the main tasks would benefit the overall impact of the effort.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The proposed future works are each logical extensions of the prior year's accomplishments. A new feature in the proposed future work (not reported in prior years) is the study of catalytic materials for hydrogen generation from alcohols and polyols. This should be a fruitful direction for future work.
- The project's proposed future work in all areas is appropriate, both technically and relative to funding level.
- The proposed future work is a straightforward extension of the 2018/2019 Phase I and II efforts. Although investigations are proposed that relate to improving understanding of hydrogen sorption, reaction sorbents, metal hydrides, and carriers, as well as support of seedling activities, some additional detail would have been useful. For example, the effort to probe structural defects on hydrogen storage properties in MOFs assumes that structural defects actually affect the storage properties. Some justification would have been helpful. Also, as pointed out in the 2018 review, it is important to understand whether the conclusion derived from the oxide work on $NaAlH_4$ ("surface hydroxides serve as low barrier sites for H-H combination and hydrogen release") is extendable to other complex metal hydrides. This is an important research issue. Likewise, a more focused effort on understanding and overcoming kinetics barriers is needed. This will require the development of a clear and rational research strategy.
- The proposed future work on activation of B-B and B-H bonds is appropriate; more focus on experimentally verifying the modeling efforts is in order. There needs to be a subsequent quantifiable measure of progress in how the understanding being gained results in improved kinetics; the capacity is nice, but if the release rates are not beginning to approach the rates required to meet practical application, then the capacity is less important. SNL has historic data on hydrogen release from bulk, nanoscale, etc., as

well as $Mg(BH_4)_2$, and is gaining more data from the present work. In the future, it would help immeasurably to measure progress of the SNL and HyMARC efforts to have a compilation of (possibly maximal) release rates, benchmarked with respect to the required release rates from the technical target.
- The proposed future work is on the safer side. For example, powder compaction and tweaks of MOFs for sorbents will not change the current trajectory in any significant ways. The team needs to take more risk. In Phase I, the responsibility of achieving the DOE targets was assigned to the seedling, while the majority of resources were spent elsewhere. It is understandable since capabilities were developed. In Phase II, the team needs to take more responsibility for changing the trajectory through setting their own goals and stepping up to help seedlings achieve targets.
- The continued work on sorbents, while good, may be a distraction to their main efforts in complex metal hydrides. It is unclear whether the work on organic carriers is the best use of SNL's expertise.

Project strengths:

- This is a comprehensive project being conducted by a highly capable and dedicated R&D team. The project is addressing important issues relevant to our understanding of hydrogen sorption processes in both metal hydrides and sorbents. The work is forming a solid foundation for development of improved materials. The project is well managed, and extensive and fruitful collaborations are augmenting the core activity. The SNL team should be commended for the extensive support being provided to seedling projects.
- The strengths of the project are its demonstrated accomplishments. The discovery of the higher volumetric capacity for UiO-67 (by approximately 55%) is a result of the ingenuity of the project team members. This result opens the door to many more discoveries. Likewise, the notion that the nanoporous framework structures play a role beyond simply maintaining the nanostructure of the hydride is a key discovery that has the potential to open many more avenues of research pursuit.
- The project's strength is in the capability of the team, and some of the significant progress made in Phase I is in developing a strong base for theory and measurements. Synthesis efforts are still somewhat weak, but seedling projects are beginning to make progress. The team coordinated well with collaborators and seedling teams.
- The team is very good, the facilities are superb, and the collaboration is excellent and effective; the project is making good progress.
- There is good integration of modeling and experiments. Expert capabilities in high-pressure hydrogen experiments can be seen.

Project weaknesses:

- A clearly defined pathway to addressing the critical problem of sluggish kinetics in complex metal hydrides is needed. Various approaches (e.g., nanoscaling, additives) are being used, but a more coherent and well-formulated strategy for generating reaction rate data would be helpful. It is hoped that a definitive statement concerning the identity of the rate-limiting step(s) in the $Mg(BH_4)_2$ reaction system can be made in the 2020 Annual Merit Review (AMR). Although not a weakness per se, as pointed out in the 2018 AMR, a more keenly focused effort is needed for determining whether the intriguing results and conclusions on the effects of oxides and hydroxides on $NaAlH_4$ hydrogen sorption can be extended to other systems (especially metal borohydrides).
- The weakness is mostly in the lack of a roadmap for achieving DOE targets and in taking more risk using the advancement made in Phase I. Overall, there are no major weaknesses in technical capabilities or execution.
- It is not certain that the liquid carrier work aligns with SNL strengths. There are perhaps too many task areas; it is possible that productivity and impact could be improved with greater focus on the modeling and experimental areas surrounding the key kinetics and thermodynamics issues of complex metal hydrides.

Recommendations for additions/deletions to project scope:

- This is not a recommendation but a general question or observation for the SNL team: it seems possible that the hydrogen carrier work being proposed by the SNL team dilutes the attention and emphasis needed

for other important tasks. It may make sense to transfer that activity to another group in HyMARC (e.g., Pacific Northwest National Laboratory).

- There are no recommendations at this point. The only suggestion for the team is to look for work already reported in the literature and develop stronger rationale for going down the same path.
- LOHC work may not be the best fit to the SNL program.

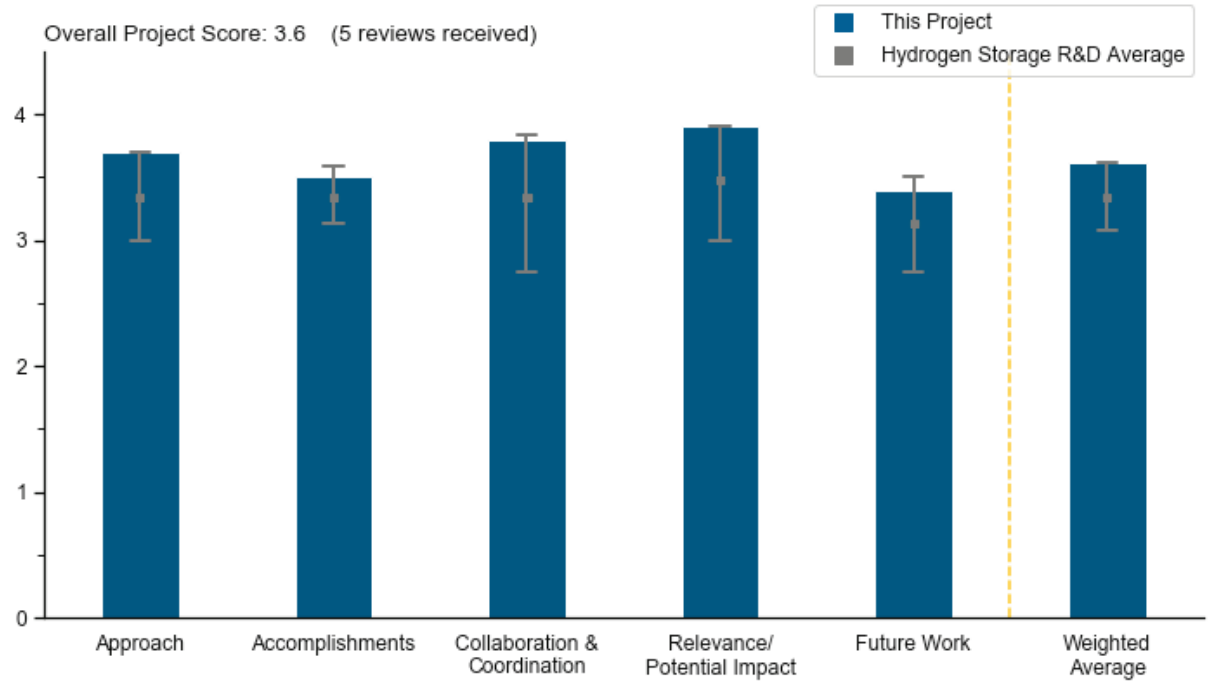
Project #ST-129: Hydrogen Materials–Advanced Research Consortium (HyMARC): Lawrence Livermore National Laboratory Technical Activities

Brandon Wood, Lawrence Livermore National Laboratory

Brief Summary of Project

The Hydrogen Materials–Advanced Research Consortium (HyMARC) is providing community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials. HyMARC team member Lawrence Livermore National Laboratory (LLNL) is conducting porous carbon synthesis; X-ray absorption/emission spectroscopy (XAS/XES); and multiscale modeling including density functional theory (DFT), ab initio molecular dynamics, phase-field mesoscale kinetic modeling, and kinetic and quantum Monte Carlo (QMC).

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.7** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach is comprehensive and addresses issues that are critical to the fundamental understanding of hydrogen sorption thermodynamics and kinetics in candidate hydrogen storage systems. The approach utilizes numerous theoretical and modeling methodologies and spans a broad range of relevant time and length scales. The approach is aligned with experimental work being conducted by other HyMARC investigators. Moreover, the project provides important and useful support for associated seedling projects.
- LLNL's approach is divided into two areas: tuning thermodynamics and kinetics. The approach is based on strong hypothesis-driven research. The use of nanoscaling to improve thermodynamics and kinetics, the adoption of an emphasis on the complexity of interfaces, and the use of eutectic as hydrogen carrier may produce important results.
- The team is making good progress on deliverables. The HyMARC theory group is guided by the needs of its partners but is also guided by synthesis work and X-ray measurement work. The team effectively assists

the rest of the consortium. The "Assess, Interpret, Model, Understand and Design" paradigm nicely sums up how the team adds value.

- The LLNL modeling approach remains firmly focused on developing an understanding of the complex energy landscape along the dehydrogenation/rehydrogenation pathways of magnesium borohydride using a wide variety of computational tools to address the multiple length scales involved. The modeling approach employed addresses the key features that influence the kinetics and thermodynamics of this material, nanoscaling and confinement being among those. The modeling effort toward understanding the reverse reactions resulting from magnesium diboride's direct use of additives and catalysts approaches the key issue of kinetics and is one of the main barriers that must be addressed for this class of materials. The modeling approach, which utilizes complex, state-of-the-art tools, is well communicated and well implemented, as usual. More thought should be given to the progress and relevance of the interaction between "additives" or catalysts and the boron nitride (BN) sheet structure. In the current model, investigators consider a naked titanium atom. This is likely unrealistic in practice; under hydrogen pressure, one would expect to find TiH_2 species, or even $TiH_{(2-x)}$ species. Therefore, the approach should be adjusted to better accommodate compounds more likely to be found under experimental conditions. LLNL also includes activity directed at modeling the electrocatalysis of hydrogen carriers. While the approach is good, this effort may be premature until more details as to the precise electrochemical system from the experimental effort are forthcoming.
- The standard test conditions comprise theory and advanced characterization. The investigators plan to improve current understanding of thermodynamics and kinetic limitations in storage materials and liquid hydrogen carriers. The project has developed a realistic plan to implement modeling and theory for solving problems identified in the hydrides (namely, borohydride regeneration, effects of nanoscaling and amorphization, and understanding catalytic and electrocatalytic additives). Validation work is under way for several portions of the computational work. This annual report discusses only briefly the advanced characterization work the team has accomplished. Since in situ kinetics is mentioned in slide 2, the topic should be better addressed throughout the presentation.

Question 2: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project has made significant inroads in understanding the role of alkali, alkaline earths, and 3D/4D transition metal dopants on MgB_2. This understanding of ionic versus covalent contribution to the surface is potentially significant for understanding borohydride regeneration. The enthalpy-versus-entropy compensation effect work related to examining the excess surface energy as a function of particle size is novel. There are few published reports that discuss enthalpy as a function of particle size in the nanoscale regime. These effects relate back to specific heat variation as a function of particle size (resulting from a change in optical phonon modes as a function of size). A 1954 report in the *Journal of the Royal Society Interface* examined these effects for titanium dioxide. Additionally, a 2016 report in the *International Journal of Thermophysics* reported on these effects on CuO, along with a loss in the Debye T^3 rule for nanoscale particles. Further work, which pushes computational frontiers on this topic, will serve the hydrogen storage community as well as the broader scientific community. It is unclear what is meant by "early results on Ti vs. Li agree with predictions" (slide 11). These results were not covered during the presentation.
- The LLNL modeling effort continues to make progress in assessing the effects of nanoscaling, mechanical stress from confinement, activation of the B-B sheets in MgB_2, and the Mg-B-H phase diagram. Aspects of the model are presented in such a way as to inform the experimentalist and suggest experimental approaches. This is highly valuable. The modeling effort is highly responsive to new experimental input and uses this input to refine the model. Overall, the team has made excellent progress in areas that support DOE metrics.
- The team is making excellent headway toward project milestones and has already made substantial progress toward many future milestones. Examples of the team's progress include the phase diagram for $Mg(BH_4)_2$, their understanding of the tuning limits of particle size and confinement, and their understanding of the impact of phase attributes on $Mg(BH_4)_2$ decomposition. Furthermore, the team has developed a brand new model for diffuse interface reactive systems. The project is currently undergoing

more interpretation, but in Phase II, more guidance is expected. Most importantly, the team interacts with experiment groups to advance in ways that neither theory nor experiment could accomplish alone.

- This research and development (R&D) activity is a vital component of the HyMARC consortium and is contributing significantly to its success. The ability to simulate and model processes at multiple time and length scales is a powerful and impressive component of the overall HyMARC activity. For example, in 2018 and 2019, the project addressed a wide range of important problems, including clustering and nucleation kinetics, developing and refining phase diagrams, predicting effects of metal dopants and other additives on bonding character, understanding metal boride decomposition pathways, assessing the role of nanoscaling on thermodynamics, and demonstrating how confinement stress can effectively destabilize hydrides and alter both thermodynamics and kinetics. The results obtained from these studies are significantly improving our understanding of the complex phenomena and processes operative during hydrogen sorption reactions in storage materials.
- The publications and presentations show that the team is wrapping up project results and making an impact on the progress of the HyMARC team. Phase diagram work is important, and though the experiment–theory feedback cycle is limited, it remains an important part of the focus. It remains to be seen whether the force field work can advance or benefit DOE targets. The discussion of metal dopants for MgB_2 decomposition began with some interesting hypotheses. The team needs to develop the theory further to extend predictive power to realistic clusters rather than restricting it to single-site dopants. The progress percentages noted are reasonable, but there are too many open threads on each. A careful recalibration of effort may be needed to achieve the Quarter 4 targets.

Question 3: Collaboration and coordination

This project was rated **3.8** for its engagement with and coordination of project partners and interaction with other entities.

- The collaboration with an experimental team is reasonable. The team is aware that progress on the models for higher-length scales will strengthen the team. The diffuse reactive interface nonlinear kinetics (DRINK) model seems somewhat disconnected from the team's efforts. At the very least, an experimental connection was not evident in the presented slides. The collaboration on symmetry-adapted perturbation theory (SAPT) potential is a good connection. The confinement stress work can be complemented by the experimental effort using coherent diffraction imaging to obtain better validation data.
- The project's interactions with seedlings are rich. These interactions include collaborations with the University of Hawaii and two National Renewable Energy Laboratory projects. New seedling interactions with Liox Power, Inc., and the California Institute of Technology have developed this year. Several other collaborations with the University of South Carolina, Tennessee State University, Georgia Institute of Technology, and Michigan State University are under way. Additionally, international collaborations are being developed.
- The LLNL modeling effort continues to be a model for collaboration among national laboratories, as well as among academic institutions. While investigators continue to make good progress on their own tasks, the LLNL effort has demonstrated that LLNL can work effectively with the seedling projects in a highly collaborative and supportive mode. The modeling effort collaborates extensively in the development of enhanced modeling tools to support the HyMARC effort. Overall, the LLNL modeling effort is a world-class effort.
- The principal investigator and the LLNL team are involved in extensive collaborations with other HyMARC core team members, other U.S. and foreign researchers, and seedling project investigators. The LLNL team is commended for their active engagement and cooperation with other members of the entire HyMARC consortium. Those collaborations are exceedingly valuable and are critical to the overall success of HyMARC.
- This group is likely the most collaborative group in HyMARC. The team has participated in many valuable collaborations both inside and outside the project. These collaborations are very beneficial to other groups and benefit this group in turn.

Question 4: Relevance/potential impact

This project was rated **3.9** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This is perhaps the most impactful of the HyMARC projects, as the LLNL effort addresses the key thermodynamics and kinetics issues surrounding the release of hydrogen from a complex metal hydride. The output from this modeling effort continues to help drive the experimental efforts, amplifying the impact of the modeling effort. The LLNL modeling effort collaborates extensively with other modeling efforts, has an excellent feedback system with experimentalists, and continues to have a high impact on progress within HyMARC.
- The work is a strong example of HyMARC's impressive progress toward technical maturity and leadership. The team has developed a new approach and hypothesis that can affect the results of the funded team and others engaged in similar research beyond the immediate team.
- The LLNL project directly supports the core mission of the HyMARC program. The research effort is focused sharply on the most relevant and consequential issues, and it is fully aligned with the overall research, development, and demonstration objectives of the Hydrogen and Fuel Cells Program.
- The project is relevant in and of itself through the results obtained, but the project also adds value to partner work via guidance of experimental theory or explanation of results. The project assists HyMARC in speeding progress toward goals and milestones that would be much slower by experiment alone.
- As prior work has shown, particularly work related to borohydride activation, computational and theoretical work provides a major impact. The annual report described little of the impact of advanced characterization (mentioned on slide 2).

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- The proposed future work continues to address important problems relevant to our understanding of the kinetics and thermodynamics of hydrogen sorption reactions. The team seeks to provide a more coherent pathway to overcoming barriers and problems. The proposed work is a reasonable and straightforward extension of the earlier studies, extending the results to more practical operating regimes. The refinement of phase diagrams for $Mg(BH_4)_2$ is important, especially with regard to changes in the phase diagram as particle size decreases.
- The team will apply their current approach to proposed future work. This is the correct decision, as their current approach is excellent. The application of more chemical intuition to the modeling of the additives could help to inform the experimentalists' approach to catalytic rehydrogenation/dehydrogenation of complex metal hydrides.
- Though the list of proposed work is not long, all items are excellent and important for realizing the strong Phase I effort. A good set of activities is under way in Phase II.
- The proposed future work is a logical extension of past accomplishments. The DRINK model will provide a method for understanding processes occurring during partial hydrogenation.
- The team outlines suitable goals in all areas. A more thorough description of the plans and the team's intended approach to handling the workload would be helpful.

Project strengths:

- A highly qualified and experienced team is conducting the project. Extensive and progress-enhancing collaboration is evident. This team is a critical component of the overall HyMARC effort. The project team has demonstrated the ability to move rapidly and effectively to address emerging problem areas. This has made the project's contributions even more valuable to the consortium because these contributions facilitate the creation of more fruitful R&D pathways for both the core HyMARC team and associated seedlings.

- The team is highly collaborative. The team provides and receives excellent feedback to and from the experimental efforts. The team is very responsive to current and changing needs. The project demonstrates a world-class modeling and simulation effort.
- This team is a strong and hard-working group that demonstrates excellent rapport with partners and external projects. The team is highly valuable to HyMARC.
- The project tackles some of the toughest computational problems that exist within the discipline. The plan to address kinetics and other nonequilibrium phenomena (including amorphization) is important.
- The strength is in the results. Therefore, the team worked hard to see the results published and ensure follow-up experiments are done. Some projects understandably originate from requests from the experimental side.

Project weaknesses:

- There are no meaningful problems.
- In Phase II, the main challenge will be to maintain the momentum. This will require effort since all of the tasks diverge in needs. As a result, the tasks generate more need for theory. Managing the proposed future tasks will be challenging, and the team may need to prioritize their effort and automate some of their workflows to expand the work to a broader set of materials. Also, the investigators are encouraged to develop more publications with a combined theoretical and experimental team in order to demonstrate the application of the modeling work and improve the overall impact.
- The only weakness of this project is the lack of results reported under a declared portion of its portfolio (in situ characterization). Since the computational and theoretical aspects of this portfolio are extremely strong, it is suggested that the team choose to either (1) address only in situ characterization in the context of using data of this type to validate computational or theoretical models/results or (2) remove in situ characterization from this project.
- A keener focus on understanding kinetic barriers and a strategy for overcoming slow kinetics in metal hydrides are needed. This applies to the entire HyMARC effort, not just the theory/modeling project. A more rational, comprehensive, and keenly focused strategy for elucidating kinetics mechanisms should be established. The kinetics problem is the “elephant in the room” for hydrogen storage in complex metal hydrides.

Recommendations for additions/deletions to project scope:

- This group is in strong demand from other parts of HyMARC and contributes in many ways. If funds are added or shifted in the future, it would be wise to consider the theory group as the recipient of more funds so the team can bring on more people (likely postdocs).
- To help future reviewers assess progress toward goals, investigators should set priorities and clearly explain how resources will be allocated.
- The application of more thought and chemical intuition to the additives modeling would result in more realistic outcomes and enhance progress in the experimental area.
- The in situ characterization section of this project is not matched well with the computational work or theory work. Either the in situ characterization should be removed, or its scope should be redefined within the standard test conditions.

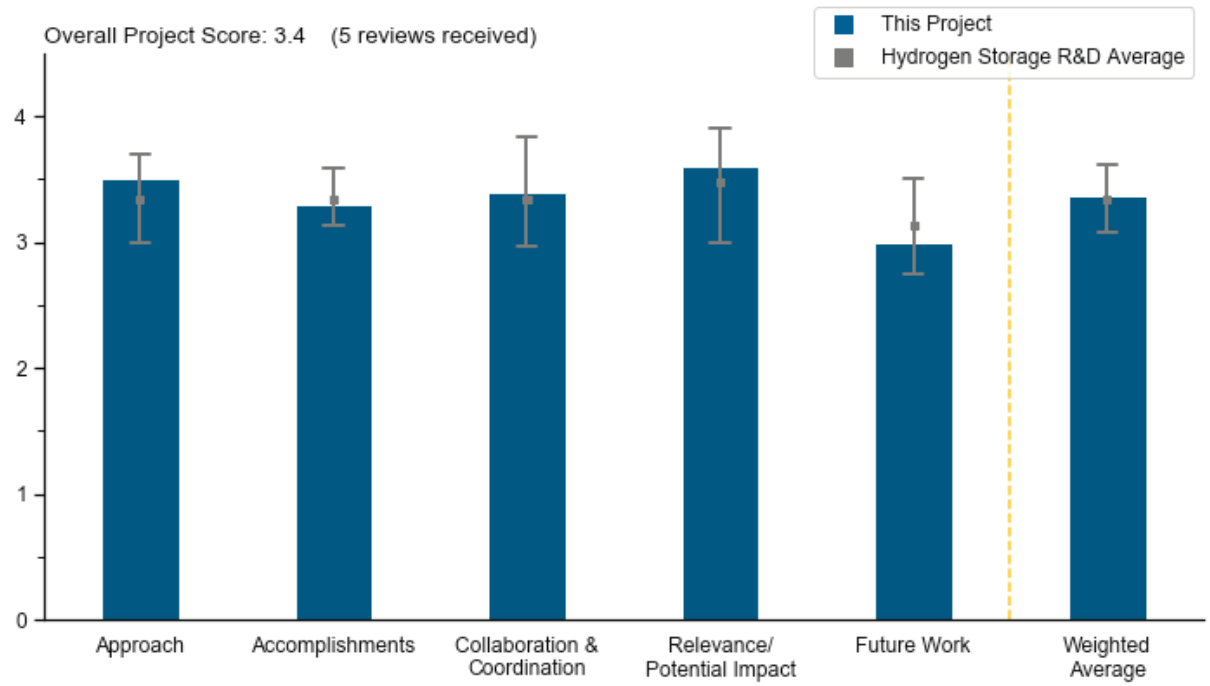
Project #ST-130: Hydrogen Materials–Advanced Research Consortium (HyMARC): Lawrence Berkeley National Laboratory Technical Activities

David Prendergast and Jeffrey Long, Lawrence Berkeley National Laboratory

Brief Summary of Project

The Hydrogen Materials–Advanced Research Consortium (HyMARC) is providing community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials. Lawrence Berkeley National Laboratory (LBNL) will (1) focus on light materials and synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements, (2) design interfaces with chemical specificity for control of hydrogen storage/sorption and selective transport, (3) explore storage concepts, (4) develop in situ/in operando soft X-ray characterization capabilities in combination with first principles simulations to extract details of functional materials and interfaces, and (5) refine chemical synthesis strategies based on atomic- and molecular-scale insight from characterization and theory.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.5** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- There are two separate pieces to the LBNL effort, the Prendergast effort and the Long effort, and the two projects are scored together as one.
    - Prendergast's approach is to utilize the LBNL Advanced Light Source (ALS) capabilities to develop in situ characterization of reacting storage materials. Sheet-like nanocarbons are used as encapsulants to nanoscale complex metal hydrides or simple metal hydrides (e.g., MgH_2). Magnesium borohydride is nanoencapsulated in metal–organic framework (MOF) cavities. The approach integrates preparation of nanoencapsulated materials with the use of ALS and conventional capabilities to characterize hydrogen release and reuptake properties of the nanoencapsulated materials. This approach is a good one, given the number of encapsulated

systems that have shown enhanced kinetics or capacities. Additional research on well-characterized materials is needed, and this project seeks to provide this research. The approach that includes the addition of metal halides to destabilize sodium borohydride would seem to have been preempted by numerous studies of metal additives that appeared in the literature 10–15 years ago. Overall, Prendergast's approach deserves a score of 3.0.

  - Long's approach is to leverage the team's expertise in preparing MOFs with open metal sites that have previously been shown to adsorb hydrogen with enthalpies approaching what is thought to be the optimal range of 15–25 kJ/mole for practical applications. To achieve this, the team is designing strategies to incorporate metal ions with open coordination sites that should have a high propensity to bind H_2 and potentially multiple hydrogen molecules. Once synthesized, these candidates are characterized in the presence of variable and high-pressure hydrogen using infrared spectroscopy and neutron scattering techniques. This is a very cogent approach, and one that is well thought out and well communicated. Overall, if it could be scored independently, Long's approach deserves a score of 4.0.

- Four major approaches were implemented to meet several Hydrogen and Fuel Cells Program goals, including the improvement of sorbents and the modification of metal hydride compounds to improve properties, carriers, and characterization. The multiple approaches greatly increase the odds of success. The goals being addressed are well defined, and the approaches have merit.
- It is key that LBNL holds the in situ X-ray absorption spectroscopy (XAS) and infrared capabilities, as well as other ex situ characterization including X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES). The development of a flow reactor for liquid carriers is under way and will be useful to other projects.
- The approach follows the work in Phase I and involves new Phase II tasks 1–4. The team is strong in operando experiments and theory. The MOF binding and multiple hydrogen molecules per site are continued in Phase II. The in situ X-ray and ex situ X-ray work backed by density functional theory (DFT) calculations was well planned and executed. The host encapsulation work and reduced graphene oxide (rGO) work needs a pathway to ramp up or ramp down. Currently, the approach does not involve any clear link to targets or metrics. So, in principle, all of the effort could continue indefinitely. Although all aspects of the approach are important for the science of reversible hydrogen storage, setting priorities can help the project's overall impact on the progress toward meeting U.S. Department of Energy targets.
- The approach is broadly based, comprising three principal research thrusts: (1) development of sophisticated in situ/operando diagnostics for probing hydrogen sorption reactions at relevant temperature and pressures, (2) nanoscaling of complex hydrides to reduce hydrogen sorption temperatures and increase rates, and (3) synthesis of MOFs containing open metal sites to facilitate increased binding enthalpies and hydrogen capacities. In addition, work on new concepts for boron-based storage and reactors for hydrogen carrier research has been initiated. The approach complements other related work in the HyMARC consortium. However, the work on nanoscaling generally lacks direction, especially with regard to overcoming cycling problems. A clear delineation of future work is absent.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team has made good progress toward the goals that have been set. All members are addressing significant barriers, and if these are surmounted, the work could yield valuable approaches or materials. The in operando and at-pressure tools developed are impressive and should be very useful in determining the mechanisms at work in advanced materials. The 21 kJ/mol binding in MOFs is a big step forward. Also, the crossover ideas of using BN (famous from hydride work) as a potential sorbent and MOFs (famous sorbents) as modifiers for $MgBH_4$ shows out-of-the-box thinking that may translate to a breakthrough.
- The project has made contributions to rGO enapsulated hydrides (produced by S. Jeong at LBNL) and has shown that the nanostructure is preserved after rehydrogenation. The team has shown differences in surface and bulk structures in nanoencapsulated $Mg(BH_4)_2$ (within UiO-67), revealing chelation of the boron with the surrounding Ni(BBY). The suite of characterization tools enables this project to make substantial

contributions to the HyMARC program. Furthermore, the project is involved in development of flow reactors for hydrogen carrier research.

- The development of an in situ/operando diagnostic capability to probe structure and reaction products at relevant temperature and pressure regimes is an important accomplishment that should greatly benefit the HyMARC program. Use of nanoencapsulants for $Mg(BH_4)_2$ confinement has been shown to facilitate dehydrogenation at reduced temperatures. However, cycling efficiency is low, and plans for overcoming kinetics obstacles were not addressed. New results on the synthesis of an MOF containing open V^{2+} sites were presented. The new MOF has an H_2 adsorption energy of -21 kJ/mol, consistent with hydrogen binding at practical operating temperatures. Similarly, an MOF containing Cu(I) sites is also predicted to be in the optimal range. This is clearly an important advancement in the development of adsorbent systems that can meet DOE storage targets.
- The team made good progress on the tasks. The V^{2+} synthesized and experimental data made important contributions. However, the Phase II effort still needs to gather momentum. More results from the new reactor from Professor Gabor Somorjai's laboratory at LBNL will be interesting. Future plans need to integrate other laboratories to achieve widespread project success and increase the quality of the results.
- Separate comments on both principal investigators' work are below.
    - Regarding the Prendergast work, progress on the rGO encapsulated materials appears to be incremental. The work on magnesium borohydride in rGO was much the same as last year. There did not seem to be enough presentation time to discuss the in situ characterization of this material in detail, nor was there any apparent progress in understanding the cycling behavior/reversibility of this material and the implications for other systems. The nanoencapsulation of magnesium borohydride in an MOF was described, and investigators witnessed a very low-temperature evolution of hydrogen at around 120°C. There was little rationale given for this approach, nor was there a discussion of the quantity of magnesium borohydride that was enclosed within the cavities of the MOF that could then be translated into an effective gravimetric capacity. Furthermore, there has been, as yet, little characterization other than some XPS. Hopefully, infrared and nuclear magnetic resonance (NMR) characterization will be implemented in the future. The statement that the material releases "mostly H_2" is insufficient to gauge whether this is interesting. The Prendergast section of the project deserves a score of 2.5 for Accomplishments and Progress.
    - The Long portion of the project successfully synthesized the first V(II) MOF, and V(II) should have a propensity to bind H_2. The team cleverly characterized hydrogen sorption on the material by using infrared difference spectroscopy to identify the H_2 as well as deuterium (D_2) stretch of bound hydrogen on vanadium. This is another accomplishment and a logical stepping stone on the way to attempting to discover open metal framework sites that can bind more than two hydrogen molecules. The accomplishments were well communicated, and it was easy to determine the good progress made. The Long section of the project deserves a score of 3.5 for Accomplishments and Progress.

Question 3: Collaboration and coordination

This project was rated **3.4** for its engagement with and coordination of project partners and interaction with other entities.

- The collaboration and coordination with other institutions is very good for both projects, and the degree of collaboration is commensurate with the size and scope of the projects.
- The team has a wide group of collaborations with excellent groups that yield value to the project.
- The project has joint publications with other HyMARC laboratories. Since the team's contribution is characterization, this is not unexpected. In the future, it would be helpful for the team to publish advances in technique development.
- Beneficial collaborations with other HyMARC investigators in most project research areas are evident. The overall HyMARC program is benefitting significantly from advanced diagnostic capabilities at LBNL. However, it is not entirely clear whether the nanoengineering activities at LBNL are coordinated in a meaningful and direct way with other nanoscaling efforts within the consortium.

- The team is strong and has good connections inside LBNL. It is unclear that collaboration with others and seedlings is used to this project's advantage. More effort is required in the area of collaboration, especially considering that other laboratories' broad use of operando work will benefit the team.

Question 4: Relevance/potential impact

This project was rated **3.6** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- Separate comments on both principal investigators' work are below.
    - Regarding the Prendergast work, nanoscaling to alter the thermodynamics and kinetics of the dehydrogenation/rehydrogenation in complex metal hydride materials has been shown by many others to be a promising pathway. This project's focus on using nanocarbon sheet-like materials is thus very relevant to this topical area. The potential impact of the work in nanoscaling is lessened by the incremental progress displayed in the presentation. The state-of-the-art characterization tools being developed using ALS capabilities is highly relevant to gaining detailed understanding of certain structural and chemical aspects of these complicated reacting systems, especially the opportunity to access X-ray spectroscopies from light elements that are of course of interest in these complex metal hydride materials. The development of operando techniques to examine these reacting materials under dynamic hydrogen conditions is very relevant to the needs of the hydrogen storage community, and the continued development of these techniques and tools can have a large impact on the area. However, it is likely that the achievable temperatures and pressures in their sample environments may ultimately limit the potential impact of these tools. If this work could be scored separately, it would receive a 3.0.
    - Regarding the Long work, developing materials that can sorb significant quantities of hydrogen at something closer to ambient temperature is a "Holy Grail" of sorbent research. Long and his group have made substantial progress in prior years, and this year is no different. The relevance of their approach to gaining adsorption enthalpies in the range of 15–25 kJ/mol is very high; if the group is successful in ferreting out MOFs that can bind multiple hydrogen molecules with the appropriate adsorption enthalpy, the potential impact on the knowledge base in hydrogen storage would be significant. There still needs to be a candid presentation on how close this approach can come to DOE targets. There is no argument that this is great science, but the practical implications need to be described in detail. If this work could be scored separately, it would receive a 4.0.
- The project is an important element of the overall HyMARC activity. The advanced characterization activities and MOF synthesis work are especially innovative and noteworthy. For the most part, the research effort is well aligned with DOE research, development, and demonstration objectives and is focused on issues that have important potential impact on the advancement of progress toward DOE targets.
- The work performed has an excellent chance of making an impact on many important unknowns in host materials design and understanding of measurements (task 4). In contrast, the theory effort seems to have slowed down somewhat. The team needs to continue some of the excellent contributions made in Phase I to ensure best practices are shared with and adopted by the community in general.
- Several major DOE objectives are well aligned with this work. This is highly relevant work.
- The relevance of the project remains high.

Question 5: Proposed future work

This project was rated **3.0** for effective and logical planning.

- The plans for future work are in line with past accomplishments and will add competencies to the HyMARC portfolio. For example, the development of measurement tools for entropy and enthalpy of adsorption will aid ST-129 in performing computationally derived enthalpy as a function of hydride particle size.
- The proposed future work is logical and promises to deliver good results. The priority assigned to the various subtasks proposed was not clear from the presentation. A more deliberate effort to engage outside

collaborations to increase the output of the team can help the team, which is already doing an excellent job in terms of strong science, synthesis, and innovation on characterization techniques.

- The future work is well designed, and clear goals are outlined. The team considers many pathways to improve chances of success on one of the many paths.
- The proposed future work in the sorbent research area is clearly stated and follows directly from the earlier work. In contrast, future work in the areas of advanced characterization, nanoencapsulation, hydrogen carriers, and boron-based storage material areas is neither presented nor discussed. This lack of discussion makes it impossible to ascertain the direction of future research in those areas.
- The Prendergast effort did not present a slide on future direction, so it is difficult to assess what directions that work will emphasize in the future. The combined future work would benefit from including an analysis of potential practical outcomes. The scientific merit of this work is abundantly apparent; however, the practical aspects require some discussion. The Prendergast section of the project deserves a score of 2.0 for Proposed Future Work. The Long effort supplied a cogent, logical path forward toward the goal of obtaining higher isosteric heats of adsorption. The Long section of the project deserves a score of 3.5.

Project strengths:

- A well-qualified team with expertise in all relevant areas is conducting work on this project. The advanced characterization and diagnostic instrumentation is world-class and provides a powerful and unique capability to the HyMARC program. The MOF research is especially innovative. Excellent progress is being made on a difficult research challenge that has a high payoff.
- LBNL provides high-performance computational tools and state-of-the-art characterization tools that take advantage of the unique capabilities of the ALS. The synthetic capabilities in open metal sites in framework materials and the characterization capabilities for hydrogen sorption under hydrogen with variable temperature capability are world-class.
- The project has many strong components that are highly exemplary. The in situ and ex situ measurements are very well executed. The synthesis of new candidates and new ideas on the table is promising. The theoretical effort has strong links to the needs of the community for MOF and host–guest materials design. It is too early to fully judge the progress of the remainder of the work.
- The strength of ST-130 is its use of both in situ and ex situ characterization techniques to address some of the most unique hydride materials (i.e., rGO encapsulated borohydrides).
- The principal investigators have strong backgrounds in their areas, great facilities, and clever approaches.

Project weaknesses:

Although it is not a weakness per se, the rGO wraps may not have good durability in containing material that alters size and requires many cycles. It will be important to check early in testing to be sure the wraps do last hundreds of cycles.

- The team needs to better integrate its effort with the other laboratories. The theory team should improve its impact by providing the wider community with data for screening on MOF and multiple binding site possibilities. It is not evident that the team engages in discussion with the University of Michigan seedling project. There seems to be a large gap between the thousands of MOFs but limited understanding of their synthesis or deeper chemical physics, and the LBNL team is trying to understand the subtle shifts in binding frequency and dependence in the new functionals studied. HyMARC investigates both aspects of MOFs, and LBNL has an excellent track record in synthesis; the project team should provide more leadership to the rest of HyMARC in identifying targets and discussing the suitability of candidates. Greater engagement by the LBNL team to provide leadership would assist HyMARC and strengthen the whole effort in certain domains.
- A number of nanoencapsulation methods are being employed to alter kinetics and perhaps thermodynamics while ensuring that the metal hydride particle size is maintained. Although some progress has been made, significant obstacles remain (e.g., a gravimetric penalty imposed by the encapsulant, poor sorption cycling, and sluggish kinetics). There seems to be no recognition of these problems, and unfortunately, the presentation does not describe future work that might address those issues. Likewise, the overall encapsulation effort seems to be largely decoupled from other nanostructuring work in HyMARC. Coordination among the related activities with other HyMARC investigators was not evident. The work on

porous BN is not compelling. In the original paper by Zhang, the adsorption binding energy for hydrogen in p-BN is very low (~65 meV/H_2). The binding energy was increased by lithium doping, but it still remained too low for practical applications. The present work does not provide a useful path forward.

- The Prendergast section of the presented materials suffers in focus and in apparent progress made. It is not clear whether this is in fact the case or whether the presentation was not constructed in a way to highlight the essential approaches and accomplishments that tie directly to HyMARC goals. The LBNL computational modeling effort was not described, and one must ask how this might be affecting experimental progress.

Recommendations for additions/deletions to project scope:

- It is too early to recommend deletions to the project scope. The scope is appropriate, and progress is reasonable for Phase II.
- It would be useful to conduct continuing evaluation of the durability of the rGO encapsulation (i.e., ensuring there is no change in rGO or in the MgBH compound composition and segregation). If the encapsulation approach fails to last, then modification of rGO or perhaps other encapsulants are needed.
- A much more compelling delineation of future work in the areas of nanoencapsulation, hydrogen carriers, and boron-based storage is needed. Future work should focus on critical issues and technical barriers. The team should eliminate the work on p-BN or present a much stronger case as to why the work should be continued.

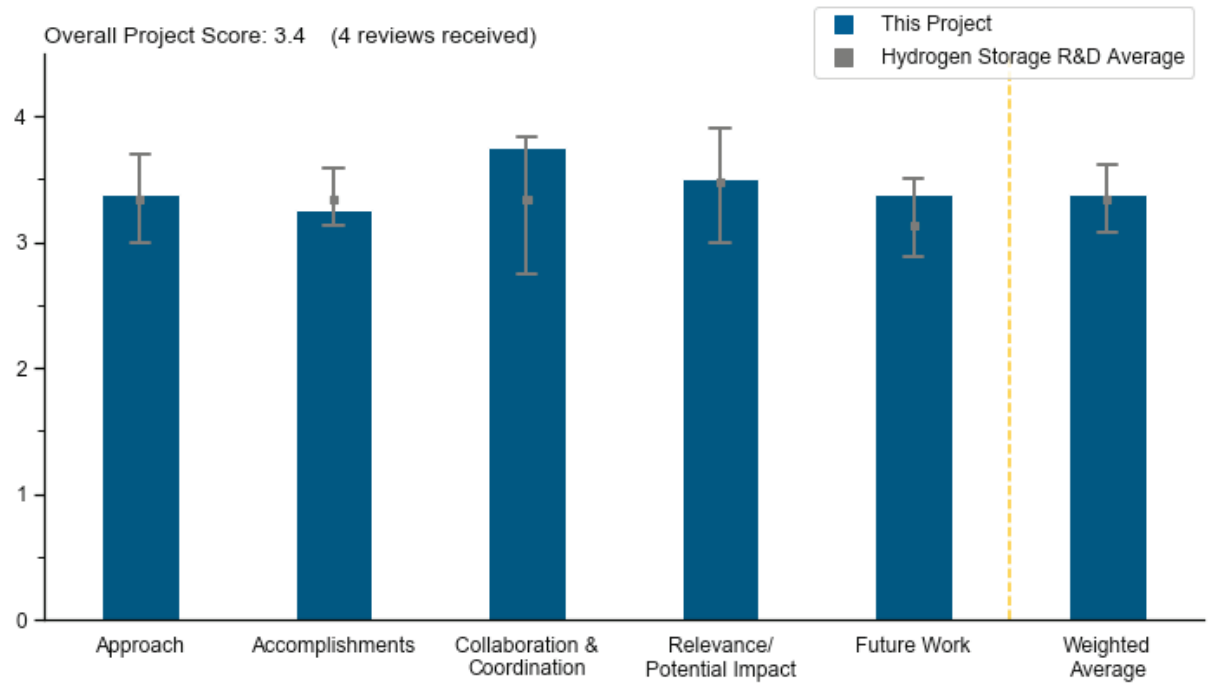
Project #ST-131: Hydrogen Materials–Advanced Research Consortium (HyMARC): National Renewable Energy Laboratory Technical Activities

Thomas Gennett, National Renewable Energy Laboratory

Brief Summary of Project

This project represents a collaboration between national laboratories to investigate the properties of promising new hydrogen storage materials and works in coordination with the Hydrogen Materials–Advanced Research Consortium (HyMARC) core team. The National Renewable Energy Laboratory (NREL) leads the collaboration, which includes Lawrence Berkeley National Laboratory (LBNL), Pacific Northwest National Laboratory (PNNL), and the National Institute of Standards and Technology (NIST). The objectives include the following: (1) develop new characterization capabilities such as nuclear magnetic resonance (NMR) spectroscopy, diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS), calorimetry, diffraction, and scattering, and (2) validate performance claims and theories critical to the design of new hydrogen storage materials.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach comprises tasks on advanced characterization and validation measurements, activation of B--B and B-H bonds in borohydrides using organic compound additives, and exploration of concepts employing adsorbents as hydrogen carriers. In addition, NREL provides characterization support and validation for HyMARC seedling projects and coordinates advanced characterization work at SLAC National Accelerator Laboratory. Although the characterization work is well focused on important problems and barriers, the materials effort seems disjointed and lacks a compelling strategy for addressing critical issues and obstacles.
    - The overall approach of the NREL project generally complements other related efforts in HyMARC. In addition, the project provides useful and important support for seedling projects. A

couple of research and development (R&D) topics that were not on a path to meet U.S. Department of Energy (DOE) goals were eliminated from the R&D portfolio in 2018–2019. This was a prudent decision that allowed the team to focus on more relevant problems.

- This is a multipronged approach with many chances to add value to DOE's program portfolio. All work is well aligned with goals. The project has clear goals. The emphasis on defining best techniques helps not only HyMARC but hydrogen storage work worldwide. Some of these are aimed at transport not onboard, which is helpful as well.
- This Standard Test Condition (STC) provides detailed thermodynamic measurement, including isosteric heat (Qst) data. These are valuable measurements for reliability in Van't Hoff measurements. This is especially important at high loading.
- The NREL approach slide contains 19 tasks to be dealt with in the near- to mid-term. This seems excessive, and in the absence of a corresponding clear rationale for each approach, it appears more like a shopping list than a well-thought-out plan to address the key barriers to "enabling twice the energy density for onboard storage." For many of these approaches, there was no high-level justification or rationale for the approach, and so it was difficult to assess the real potential of each item in the list to map onto a HyMARC thrust area, leading to progress toward DOE goals.
    - Here are examples of instances where a clear justification would help. The Task 2c approach did not set apart how NREL was going to distinguish the approach and potential outcomes from the effort of Severa et al. in exploring tetrahydrofuran (THF) as a donor ligand in the magnesium boride–borohydride system. Other examples lie in the hydrogen-carrier-focused activities. In the absence of DOE targets for hydrogen carriers, NREL could and should describe the potential for improving the quantity of hydrogen to be transported versus, for example, methylcyclohexane as a model benchmark for two-way carriers. The NREL approach for the porous liquids did come close to this by describing the potential benefits but did not address some type of analysis for each approach proposed (sorbents, BH_4/ionic liquids, etc.) that could prioritize the various efforts. This is true not just for the NREL effort in hydrogen carriers but within the associated HyMARC projects in general. In the absence of technical targets, an improved approach would factor in such prioritization.
    - An exception to this deficiency in developing a rationale for proposed work is in the work of Parilla, Hurst, et al. in describing the approach to solving the difficulty and errors in extraction of isosteric heats from adsorption data. The approach here is well defined, the relevance and impact were made abundantly clear, and progress was demonstrated.
    - Another exception was the clear rationale and justification given for the approach to the preliminary investigation of the plasmonic heating/hot electron project for obtaining "on demand" hydrogen release from magnesium borohydride.
    - If the latter two examples were not the exceptions, the NREL approach would receive a 3.5 or a 4.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Good progress was made in most project areas. Most notably, a better understanding of isosteric heat measurements was developed using a variable pressure-composition-temperature isotherm (PCT) apparatus. This reduces the possibilities for confusion, bias, and misinterpretation of adsorption results. A novel method for activating B-H/B-B bonds in $MgB_2/Mg(BH_4)_2$ using THF incorporation via vapor phase transport facilitated better control of THF concentration, thereby providing means to understand the role that the organic additive plays in enhancing hydrogen sorption reactions in the Mg-B-H system. New work on the use of adsorbents as hydrogen carriers ("porous liquids") is being explored as a means to deliver hydrogen-containing molecules in a more efficient and higher-capacity format. Advanced diagnostic capabilities at SLAC are now part of the core HyMARC effort. Although no results were reported, these capabilities will undoubtedly provide the consortium with a more robust and powerful suite of diagnostics for all aspects of the experimental effort. The NREL effort also provided beneficial support for multiple seedling projects. In general, the HyMARC program should be commended for its continued support of and contributions to seedling projects. The collaborations have been effective in accelerating progress on those projects.

- In addition to thermodynamic measurements, the group is working on understanding THF adduct in $Mg(BH_4)_2$. THF is introduced to $Mg(BH_4)_2$ by gaseous route. This is done to limit the amount of THF that is adsorbed. The vapor pressure of THF was controlled to ensure that it was bound in the structure (and not in excess). The results indicated that THF adducts alter the desorption pathway for hydrogen.
    - Additionally, unique work on liquid carriers is taking place within this project. The liquid phase is a "porous liquid" whereby porous nanoparticles are dispersed in a solvent. This work seems to be quite early. However, the potential for a different type of liquid carrier is promising here.
    - One of the major innovations in this portfolio is the release of hydrogen by on-demand heating of plasmonic nanoparticles. This work enables the use of a lower power source for hydrogen release. This is similar to ideas published on hydrogen release using microwave irradiation back in 2009 (see https://www.mri.psu.edu/sites/default/files/file_attach/212%29.pdf).
- The accomplishments of the work by Parilla, Hurst, et al. are top-notch. Their exacting work enables the adsorption community to extract isosteric heat information from data and to communicate results in this area more effectively and accurately, further enabling an "apples-to-apples" comparison of literature results.
    - The very preliminary results from the plasmonic "on-demand" release of hydrogen from magnesium borohydride is intriguing. The community awaits further characterization and quantification of how much hydrogen can be extracted per light pulse per gram of material and other details such as purity of hydrogen, etc. Also of interest is the additional characterization of the material. It is uncertain whether any chemistry occurs upon the deposition of TiN onto the borohydride and, if so, how that would influence the plasmonic response. It is intriguing, and it will be interesting to see more progress in this area.
    - In the area of developing new hydrogen carriers, NREL has made good progress in the synthesis of a few systems. However, it is not known how these systems stack up against other proposed two-way carriers in regard to energy efficiency, capacity, reversibility, etc.
- The project is making good progress in line with the plan. The research team developed cryo-PCT-based isosteric heat measurements, which will help develop better sorbents. At the same time, the team developed a technique to avoid temperature term bias and thus improper results. At the opposite end of the spectrum, the team developed a high-temperature PCT for accurate measurements in high-temperature systems.
    - The project improved the MgB system with precise amounts of THF to lower desorption temperature. Though more progress will be needed, this is still a new avenue to pursue. The project showed that low-energy light can be used to release hydrogen from the MgB system via the TiN layer.

Question 3: Collaboration and coordination

This project was rated **3.8** for its engagement with and coordination of project partners and interaction with other entities.

- Solid collaborations with HyMARC core and seedling projects and external investigators are evident. The project is providing HyMARC with excellent support and expertise in advanced characterization, test protocols, and validation. The principal investigator (PI) serves as a co-leader of the recently consolidated consortium. This will help to ensure the coordination and management of the technical efforts in such a broadly based and multifaceted activity.
- Many collaborations are ongoing with NIST, SLAC, LBNL, PNNL, Sandia National Laboratories, and Lawrence Livermore National Laboratory team members. Additionally, collaborative projects are ongoing with Colorado School of Mines, University of Hawai‘i, and University of Geneva (Hans Hagemann and Angelina Gigante).
- There is significant collaboration inside and outside of the HyMARC group. There are collaborations with high-grade researchers—and in ways that help the project.
- In the work on the use of THF as a donor ligand to activate bonds in the Mg-B-H system, it was not clear if NREL was collaborating and/or communicating with the University of Hawai‘i or the PNNL groups. NREL has been active in supporting the needs of the seedling projects with NREL characterization capabilities. It appears the degree of collaboration outside of HyMARC is commensurate with the level of funding.

Question 4: Relevance/potential impact

This project was rated **3.5** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This project is going after some of the most innovative ideas in materials development. That means there is potential for high-risk–high-reward research. Currently, the porous liquids and on-demand hydrogen are developments unique to the HyMARC program led by this group. Additionally, the detailed thermodynamic measurement work is of high value and general interest to the hydrogen storage community.
- The project is an important component of the overall HyMARC activity. The project directly supports the goals of the Hydrogen and Fuel Cells Program. The advanced characterization capabilities and expertise at NREL provide DOE with a vital resource. The consolidation of the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) and HyMARC programs has created a more sensible and natural "home" for the NREL materials efforts. However, additional work still needs to be done to more firmly establish the relevance and importance of the materials activities.
- There is a heavy emphasis on developing measurements and techniques to ensure the rest of HyMARC and, by extension, researchers worldwide obtain precise and dependable data. This is critical in an efficient march toward the DOE goals. Also, the project is completing highly relevant work in the new carriers area that will matter in the transport of hydrogen.
- The relevance and impact of the work by Parilla, Hurst, et al. are high, as the work has elucidated where errors can arise in the characterization of certain aspects of gas sorption on solids, and has addressed improvements and prescribed improvements in techniques and sorption instrumentation to mitigate these errors. The work is really first-rate.
    - In the new area of hydrogen carrier work, the proposed future work includes developing an analysis of what the thermodynamics "window" needs to be for effective hydrogen carriers. The current work would have likely been more impactful with some sense of prioritization had the researchers done this task first and then considered candidate systems. Absent some set of metrics, it is difficult to assess whether the systems the team has chosen will be relevant.
    - NREL's impact in the area of using THF as a donor ligand to alter the kinetics of hydrogen uptake/release in the Mg-B-H system is difficult to assess without a cogent discussion as to how NREL is starting where the University of Hawai'i left off or how the preliminary results contrast and/or amplify the results of Severa and PNNL.

Question 5: Proposed future work

This project was rated **3.4** for effective and logical planning.

- NREL's role in providing improved methodologies and validation of sorption measurements of promising adsorbents is clearly a high-priority item for the hydrogen storage community.
    - The future work on hydrogen carriers will now benefit from the inclusion of a preliminary thermodynamics analysis of carrier properties, coupled with the LBNL and Argonne National Laboratory technoeconomic analyses, which are apparently ongoing. NREL's future work in carriers may benefit from applying these analyses before getting too far down the road on carrier synthesis and characterization.
    - There was not a mention of what the future plans are for this intriguing plasmonic-induced release of hydrogen from magnesium borohydride. It is to be hoped that a thorough characterization of the materials and the products can lead to more interesting results in this area.
- The future work capitalizes on earlier results with further optimization and introduction of new characterization techniques. These are all useful directions. At this stage in the HyMARC portfolio for this project (at the start of Year 2 of 5), it may be too conservative of a plan (i.e., to optimize and characterize the novel materials developed in Year 1 or earlier years). Because the team is less than halfway through its five-year grant period, additional exploration of innovative materials concepts could be more suitable (particularly given the innovative ideas put forth so far). Support for seedlings is also planned for the future. This is also good.

- The future work is a logical extension of the prior studies. It is concerning that the second bullet in slide 23 (future work) describes further developments of polyetheretherketone (PEEK) materials. However, apart from a statement that a no-go decision was made on compaction, PEEK materials were not mentioned in the presentation. It is not clear why the metal–catechol modified materials are being explored or what the impact would be if successful. Also, a more compelling argument for the inclusion of the plasmonic hydrogen release activity would be helpful. Although it is an intriguing result, the impact and value to the HyMARC activity, or where or how the plasmonic hydrogen release activity fits in, are not especially clear.
- There are suitable and broad future work plans with gates.

Project strengths:

- Thus far, the merger of the HyMARC and HySCORE efforts appears to be successful—kudos to both teams for making a relatively seamless transition to a less complex and confusing organizational structure. The NREL team brings important expertise and experimental capabilities to the HyMARC core team and seedling efforts. Incorporation of SLAC into the overall effort should provide access to additional sophisticated diagnostics.
- The NREL work of Parilla, Hurst, et al. on sorption methodologies and validation is world-class.
- Truly, this project stood out among most of the others for the innovative concepts in materials development.
- The project strengths include facilities, people, and alignment with laboratory strengths. The project activities are excellent.

Project weaknesses:

- It is not clear where the work on PEEK materials is heading. Apart from a no-go decision regarding compaction, PEEK materials were not highlighted in the presentation. However, the PEEK work is included in the Future Work slide. Clarification and justification for continuing that effort are needed. Although the results on the new plasmonic hydrogen release activity are interesting, a more compelling justification regarding the potential impact of that work and how it fits into the overall HyMARC mission should be provided.
    - Overall, the materials work seems to represent several largely fragmented and uncoordinated activities. The PI is urged to work closely with other members of the HyMARC team to create a unifying framework for the materials efforts to ensure that they are truly relevant to the overall mission of the consortium.
- The future work could be more ambitious on the materials development side of things (at this stage). Much of the future work presented in slide 23 is optimization and validation.
- The use of photonic material as onboard with a flow system is fraught with difficulty. It may not be worth the effort, and the team should at least consult the Hydrogen Storage Engineering Center of Excellence results in this area before trying. The project should continue to work on the material.
- It is unclear where the THF/Mg-B-H system is heading, and this effort could use better justification to strengthen the case for continued research.

Recommendations for additions/deletions to project scope:

- Without a more compelling justification for continuing the work, a no-go decision on PEEK materials is recommended. It is unclear whether the NMR capabilities at NREL are available for more extensive support of the HyMARC activities. It is apparent that the overall HyMARC effort is in serious need of additional NMR support. Perhaps NREL could provide that support.
- The project team should consider a reasonable design for a dehydrogenation unit using the photonic material at a station or other use point so that the material is a carrier.

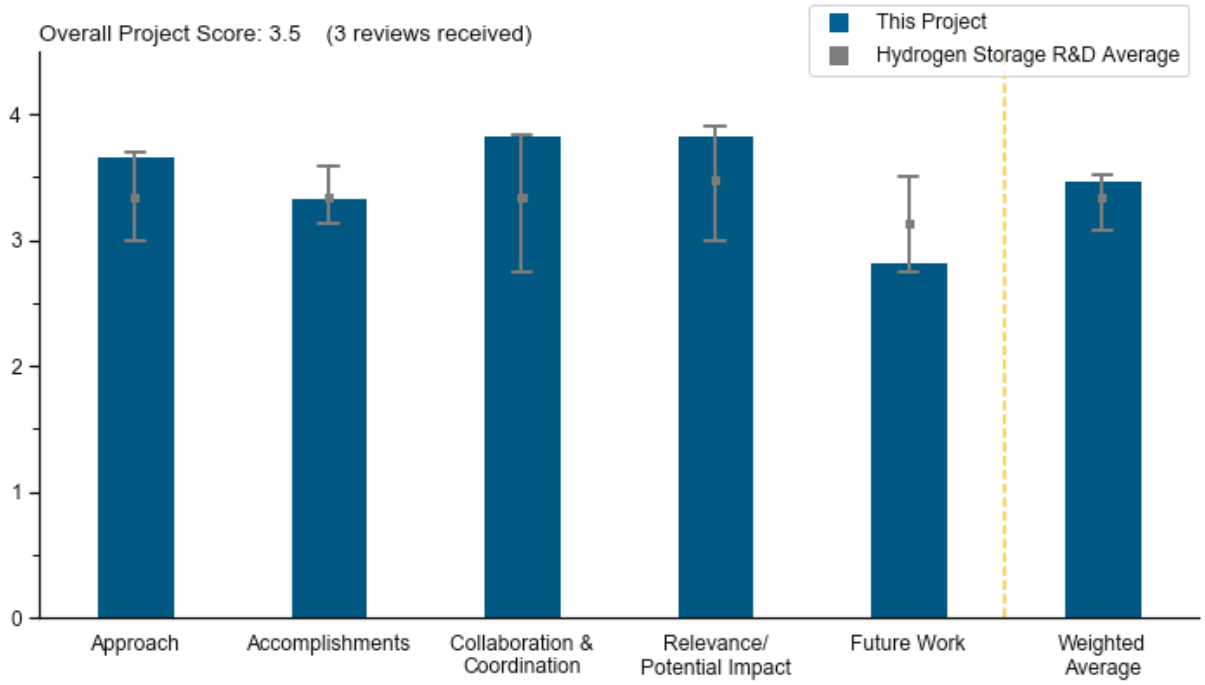
Project #ST-132: Hydrogen Materials–Advanced Research Consortium (HyMARC): Pacific Northwest National Laboratory Technical Activities

Tom Autrey, Pacific Northwest National Laboratory

Brief Summary of Project

This project is part of a collaboration between national laboratories to develop new characterization capabilities to investigate the properties of promising new hydrogen storage materials. The project works in coordination with the Hydrogen Materials–Advanced Research Consortium (HyMARC) core team. Pacific Northwest National Laboratory (PNNL) will focus on nuclear magnetic resonance (NMR) spectroscopy and calorimetry to complement parallel efforts at other national laboratories. The project will also work toward validating claims and theories critical to the design of new hydrogen storage materials that show promise.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.7** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach is broadly based and comprehensive, and it addresses issues that are important and relevant to U.S. Department of Energy objectives. PNNL serves as the focal point for the emerging effort on hydrogen carriers. The principal investigator (PI) and collaborators have formulated a solid research plan devoted to development of novel concepts and materials. This will undoubtedly be a critical research and development (R&D) area for HyMARC in the future. The approach on complex hydrides focuses the role of organic additives on sorption reactions in the Mg-B-H system. The effort augments the work at the University of Hawai‘i and elsewhere in HyMARC. The PNNL team brings valuable synthetic chemistry and mechanistic understanding to this potentially important research topic. Advanced synthesis characterization capabilities (e.g., high-pressure reactors and high-pressure in situ NMR) are being used effectively to measure thermodynamic properties, rates, and cycling efficiency and to identify/characterize intermediates in all experimental elements of the project. In addition, the approach includes extensive

support for seedling projects. (Seedling support is a hallmark of HyMARC; PNNL and the entire HyMARC team are commended for supporting and reinforcing the seedling activities in such a valuable way.)

- The PNNL approach utilizes a demonstrated close coupling of computational modeling with experiment. PNNL's approach is a chemical sciences approach, which is highly complementary to the general materials science approach of the overall HyMARC effort. PNNL brings to bear its capabilities, expertise, and deep knowledge of chemically reacting systems to provide chemical intuition and insight into the breadth of topics involved in storage of hydrogen in complex metal hydride compounds. PNNL also brings its world-class NMR capabilities to bear on HyMARC problems.
- The general theme here is to pose a good question and then to use the team or find expertise and partnerships to find the answer. This team is extremely efficient at conducting this process. This has led the team to extremely useful findings in the borohydrides. The team is poised to make new discoveries in the liquid carriers.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- PNNL's computational modeling of the energy landscape of the multiplicity of possible chemical reaction networks interconnecting magnesium borohydride with one of the intermediate products, decaborane, has provided new insights into the most likely pathways, and then suggests experimental approaches to validate potential pathways via spectroscopic techniques. These are important contributions to understanding the initial steps in dehydrogenation of magnesium borohydride and also understanding where the thermodynamic "traps" lie.
    - Using experiments supported by the laboratory's capability in solid-state NMR, PNNL has found that the presence of MgH_2 influence leads to the lower-temperature, lower-pressure regeneration of magnesium borohydride from magnesium triborane. This piece of experimental work contributes important additional experimental evidence to support a piece of the puzzle regarding the energy landscape of the Mg-B-H system in the early stages of dehydrogenation or, conversely, the late stages of regeneration of dehydrogenated material. This presumably allows for the "benchmarking" of the PNNL computational modeling effort that is ongoing in parallel. In parallel, PNNL is performing a detailed "postmortem" of the reaction products from the regeneration of magnesium triborane to look for minor products that arise during reaction. This is anticipated to again provide additional support to the development of more detailed understanding of the energy landscape that drives the chemical reaction pathways in the rehydrogenation of light polyboranes, as well as the early stages of dehydrogenation.
    - PNNL is conducting collaborative work with the Severa et al. group at the University of Hawai'i on how the influence of a donor ligand such as tetrahydrofuran (THF) can alter reaction pathways. This work is providing insight into the role of THF. How the ratio of THF:$Mg(BH_4)_2$ influences the recyclability has been explored in some detail using the combination of X-ray powder diffraction (XRD) and variable-temperature, high-field NMR.
    - In the area of hydrogen carriers, an H2@Scale activity, PNNL has taken on a leadership role. A technoeconomic analysis (TEA) activity has been initiated with Lawrence Berkeley National Laboratory (LBNL) and Argonne National Laboratory (ANL) that will, in the future, focus any R&D effort that may be required. This activity needs to be accelerated, as there are many nascent experimental activities under way across HyMARC, and it is not clear that these independent activities are prioritized or justified against technological needs or with regard to technological potential. ANL has shown in a preliminary analysis that "one-way" carriers may be more economically viable than "two-way" carriers; PNNL appears focused on one-way carriers, which may be the right niche to distinguish HyMARC's approach in this area from the many others that are cropping up. PNNL, LBNL, and ANL need to get out in front of this—quickly.
    - PNNL's activities on one-way carriers appear intriguing, as the use of electrochemical approaches to regenerate carriers and to release hydrogen at pressure (electrochemical compression) appears intriguing; but these activities must, in the near future, be backed up by detailed TEA of the round-trip costs and efficiencies from "well" to city gate. While little of this electrochemistry is new, the

utilization of non-hydrogen pathways and electrochemical compression of the hydrogen released and the integration of these processes may be novel.
    - In PNNL's work on the computational modeling of hydrogen sorbed in metal containing open framework materials, it was not clear if this was being done in collaboration with the LBNL effort (J. Long). While the work is of high quality and topical, it appeared to be a bit of an outlier in PNNL's overall approach in supporting HyMARC activities. The reviewer-only slides provide additional information on the collaboration with LBNL using PNNL's high-pressure Magic Angle Spinning (MAS) NMR capability and also looking at hydrogen diffusion in open framework materials using pulsed field gradient (PFG) techniques. More details of the extent of the collaboration will likely emerge as this activity matures, and perhaps it will include this tie to the computational modeling effort at PNNL and how it fits in with what M. Head-Gordon is doing with J. Long at LBNL.
- Solid progress was made in all project areas. The PNNL team is off to a great start on hydrogen carrier development. The team members have proposed a range of novel concepts and approaches, and they are working in close collaboration with other HyMARC investigators to develop those ideas further and to identify critical materials needs and challenges. The PI is working closely with other collaborators to understand the role of organic additives on Mg-B-H sorption reaction kinetics and cycling efficiency. This is currently one of the more promising approaches to improving reaction kinetics, and the PNNL team is providing vital chemistry expertise and experimental resources to the effort. In related work, both theoretical/modeling and experimental work (mainly in situ NMR) are being used to understand reaction pathways and ways to activate B-B and B-H bonds. A candid assessment of remaining challenges and barriers serves as a useful means to motivate the technical activities.
- The research group is very good at locating partners and establishing collaborations for characterization. An effective example of this is using NMR to understand what is occurring in borohydrides. It was discovered that the B-B bond activation rate is limiting for re-hydrogenation. Coupled with thermodynamic modeling and solution NMR, these studies have provided researchers with the ability to tackle borohydride re-activation and reaction pathways.
    - The borohydrides are just one example. Another is the use of chemical hydrides (hydrogen carriers) such as formic acid. Earlier work done on formic acid showed that catalysts such as Pd (see Krame, Levy, and Warshawsky, 1994) and iron (see Laurenczy, *Science* 2011) are extremely important to the formate/bicarbonate cycle and to H_2/CO_2 production. This work instead utilizes electrocatalytic regeneration. Little is discussed related to the catalysts that were effective (slide 18).

Question 3: Collaboration and coordination

This project was rated **3.8** for its engagement with and coordination of project partners and interaction with other entities.

- The group is very good at locating partners and establishing collaborations for characterization. The team has developed international partnerships with the Korea Institute of Science and Technology, the Association for Iron & Steel Technology, and the Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research (HZG). The interaction with seedlings (the University of Hawai'i) on borohydride regeneration is one of the high-profile outcomes of seedling support. Other interactions with seedlings seem to be under way in the form of thermodynamic modeling and NMR characterization.
- Extensive and valuable collaborations with HyMARC core and seedling activities and with external R&D institutions are evident. Those collaborations are extending the scope of the investigations and accelerating progress. The technical effort is well managed and coordinated.
- A forte of PNNL's efforts in support of HyMARC is their demonstrated participation in collaboration, both within HyMARC and with external global scientific collaborations. The quality of several of the collaborations is confirmed by the number of joint publications that have arisen.

Question 4: Relevance/potential impact

This project was rated **3.8** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- The project is an important component of the overall HyMARC activity. The project is focused on issues that are directly aligned with the goals and objectives of the DOE Hydrogen and Fuel Cells Program. The inclusion of PNNL in the consolidated HyMARC effort brings valuable chemistry synthesis expertise, mechanistic understanding, and advanced diagnostics capabilities to the consortium.
- The PNNL effort in computational modeling of the early stages of magnesium borohydride dehydrogenation (or the reverse reactions) is highly complementary to the theory effort at Lawrence Livermore National Laboratory (Wood et al.). These parallel activities have potential to gain insights more rapidly into the underlying chemical and physical barriers that limit the kinetics of hydrogen release and reversibility in the Mg-B-H system.
- The project set has already made a major impact on understanding borohydrides and is poised to lead in liquid hydrogen carriers work. So long as the team has the ability to attract and assemble the best expertise (worldwide) on the topics it pursues, it will continue to make great impacts.
- PNNL's expertise in chemistry and reaction mechanisms, collaborations, and experimental capabilities have a significant impact across many HyMARC activities and are accelerating progress.

Question 5: Proposed future work

This project was rated **2.8** for effective and logical planning.

- Liquid hydrogen carriers is a new component of the portfolio. It is a relatively new area and has the ability to encompass work in the hydrides (with adduct formation) to formic acid. The researchers have the relevant tools necessary to tackle these problems. Characterizing the amorphous phases formed by XRD or PDF (Pair Wise Distribution Function) could be added as a logical next step.
- The proposed future work flows logically from the prior research efforts. The work on the Mg-B-H system remains focused on developing understanding of the effect of side reactions, byproducts, additives, etc. on the reaction pathways that relate to hydrogen release and reversibility and kinetics limitations in this material. The future work should include some urgency in developing a detailed TEA to help guide HyMARC experimental activities in hydrogen carriers to enable prioritization and down-selection criteria. Ideally, this would have occurred prior to starting an experimental program, so now the team must catch up quickly.
- Unfortunately, the future work is not summarized in a single slide. Although some future plans are incorporated into the narrative in a few selected slides, it is difficult to extract that information for the entire project. It is probably safe to assume that slide 21 (Remaining Challenges and Barriers) provides the motivation for future work, but what will actually be done to address those obstacles remains uncertain in most cases. It would be helpful to include a Future Work summary slide that succinctly states the future work in a compelling way.

Project strengths:

- The research group has assembled a unique toolset for pursuing advanced materials. The tools include solid-state and solution NMR and thermodynamic modeling and experimental data. The scientific output has resulted in numerous publications in 2018 and 2019 alone. The group is collaborating with those from around the world who can bring insights to the problems under study. It is a wonderful idea to categorize the liquid hydrogen carriers more broadly (as in, to include adducted borohydrides) and to pursue them with the same tools as other liquid carriers (i.e., formic acid). This section of the portfolio appears to have risen out of the ammonia work done in 2004–2010—but is now extended to more promising liquid carriers.
- The PNNL team is experienced and highly qualified. The team brings valuable synthetic chemistry expertise and mechanistic understanding as well as advanced and novel characterization capabilities to HyMARC. The team has demonstrated the ability to adapt quickly and shift to new R&D problems and opportunities. This is contributing to the overall value and importance of the PNNL effort to HyMARC.

The PNNL team has assumed the leadership role in HyMARC for hydrogen carrier work. The involvement of experienced chemists at PNNL in that technology area will undoubtedly pay big dividends for HyMARC.

- The PNNL effort provides a good deal of chemical expertise, intuition, and state-of-the-art NMR characterization capabilities for gaining a detailed understanding of the critical bond-breaking and bond-making pathways, where potential kinetics barriers may exist, and where thermodynamics traps may lie in the very complicated Mg-B-H system. These are important strengths of the project and, coupled with PNNL's ability to coordinate and integrate the laboratory team's efforts and results with those of others within HyMARC, amplify the project impact.

Project weaknesses:

- The activities themselves have few weaknesses. The project reporting has many.
    - For example, on slide 9, it is impossible to read the x-axis for the data presented in the graph on the right-hand side of the page.
    - Slide 14 mentions TEA without any definition. Within this context (of adding liquids to borohydrides and also using these liquids directly as hydrogen carriers), TEA could represent triethylamine. It was not until the review presentation that TEA was defined as technoeconomic analysis. Since an entire slide title (slide 14) is about TEA (with the take-home message related to TEA), it would have made sense to spell this out earlier.
    - There is little time in the review to provide background and context to the studies; however, it would have been useful to mention earlier work done (since 1994 by Krame, Levy, and Warshawsky and since 2011 by Gabor Laurenczy) on the liquid hydrogen carriers under study in this project.
- A more complete and compelling presentation of future work in all PNNL project areas is needed. Also, there is a general comment for HyMARC (not a PNNL project weakness, per se): As pointed out in other HyMARC team reviews, slow kinetics remains the most critical obstacle to adoption of high-capacity complex metal hydrides for practical hydrogen storage applications. Although multiple research efforts (both theory and experimental) are being devoted to the problem, there is no clear strategy that rationally and objectively addresses the critical issues. PNNL is strongly urged to work closely with the rest of the HyMARC team to develop a coherent and rational pathway to addressing this critical challenge.

Recommendations for additions/deletions to project scope:

- It is apparent that the overall HyMARC experimental effort is limited by the lack of NMR instrumentation. Although PNNL's NMR capabilities are powerful and are advertised as important support resources for the HyMARC program, it seems that those capabilities are not readily available in a dedicated and timely way for HyMARC work. The PNNL NMR system(s) also support other major programs, so HyMARC work may be getting lower priority. Perhaps the PNNL project team and DOE Hydrogen and Fuel Cells Program could exert pressure on PNNL management to make these valuable resources more readily accessible to HyMARC. Clearly this is a thorny political issue, but nonetheless, it is crucial to find a way to free more NMR time, either at PNNL or elsewhere, to support HyMARC.
- It is recommended that PNNL, in its leadership role in the hydrogen carrier HyMARC effort, accelerate the TEA activity to provide guidance to the experimental efforts that are arising. Targets or down-select criteria must be determined quickly so that experimental efforts are not wasted on carrier concepts that cannot lead to the desired outcomes.

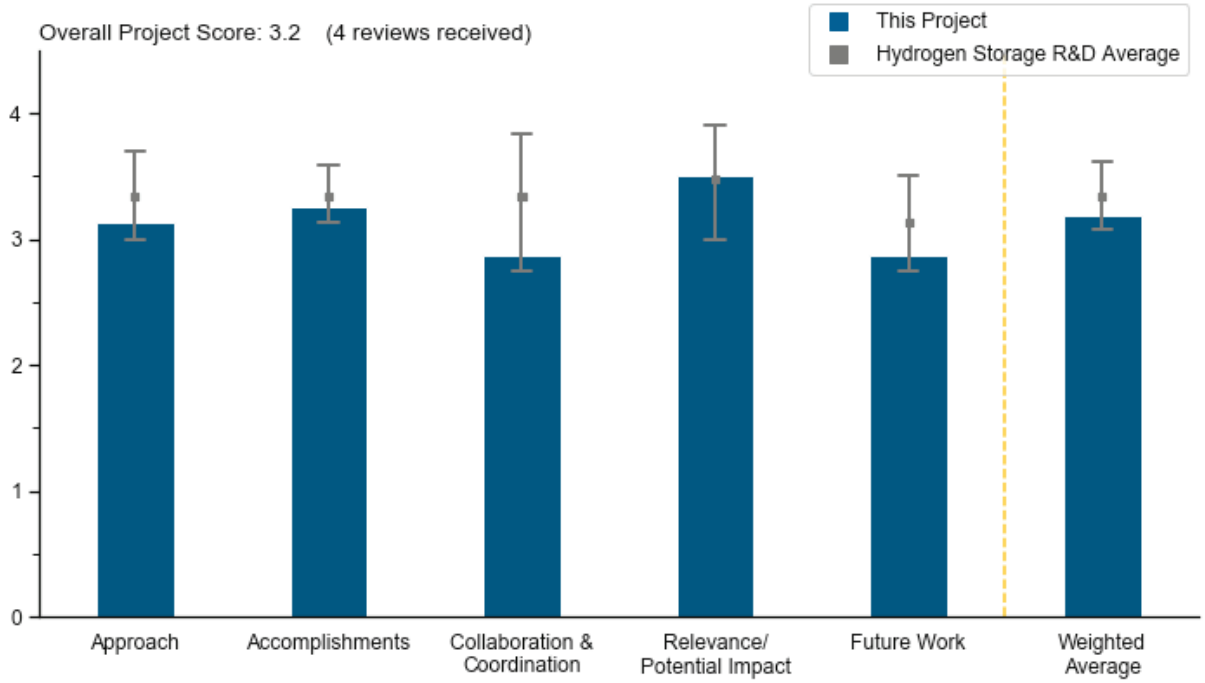
Project #ST-137: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Electrolyte-Assisted Hydrogen Storage Reactions

Simon Jones, Liox Power

Brief Summary of Project

The project will address kinetics of multiphase hydrogen storage reactions that are severely limited. The project seeks to overcome kinetic barriers of hydrogen storage candidates with high capacities (and appropriate thermodynamics) for polymer electrolyte membrane fuel cell use that otherwise contain multiple solid phases that must nucleate, grow, and be consumed during cycling. The reaction rate and transport of solid-state reactions are limited by relatively small solid–solid interfacial surface area. The project will instead use electrolyte-assisted hydrogen storage reactions that facilitate transport and enable the reaction to occur over the full surface area that is exposed to the electrolyte. Salt and borohydride electrolytes, which are the most stable for this application, will be used to promote solubilization and diffusion of species relevant to hydrogen storage release and uptake. The work will improve understanding of hydrogen physisorption and chemisorption.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.1** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach for this project is novel and could provide use for previously problematic materials. The approach does well to consider the full material density, which will provide a more honest performance of the material. Investigating combinations that can operate at a lower pressure, allowing the project to bring the testing in-house instead of relying on other laboratories, will probably save cost and increase throughput.
- The project takes a unique approach to overcoming kinetic barriers in hydrides through the addition of molten salts. This approach is analogous to additions of tetrahydrofuran (THF). However, THF forms adducts with hydrides that are not easily reversed. The use of molten salts could avoid this problem.

Additionally, fewer organic solvents are available that are compatible with the hydrides relative to the selection of molten salts.

- The approach attempts to address the key barrier to the storage of hydrogen using complex metal hydrides, i.e., the kinetics of release and rehydrogenation of spent material. In previous results from this project, the effect of solvents was shown to overcome, in part, intra-particle and particle surface diffusion limitations of reacting species in multiphasic, solid-state materials such as in the Mg-B-H system. To follow on, the team's approach will involve trying to optimize (i.e., minimize) the amount of solvent required to mitigate, to the extent possible, the weight penalty of adding solvent to the material. Additionally, the team proposes to screen additional materials that exhibit kinetics limitations and have hydrogen contents of >4 wt.%. In its published work, the team has demonstrated that the presence of a solvent/electrolyte in a model system (MgH_2/Sn) improves the hydrogen release rate by 25 times. This result is impressive but perhaps one to two orders of magnitude short of the rates required for onboard storage applications using a more realistic higher-capacity material. More work on higher-capacity materials is warranted, and so this approach continues to be of interest. The approach for exploring molten low-temperature eutectics as solvents is well thought out and is backed up with careful considerations of the prevailing thermodynamics constraints to select potential candidates for additional study. In a third approach, the team proposes to evaluate electrochemical reactions to supplement or supersede thermochemical approaches to hydrogen release from complex metal hydrides. This approach needs better definition as to what is intended; for example, the team does not explicitly define a source for the electrochemical driving force. A detailed schematic of the process and an energy balance is needed to describe this opportunity to supersede onboard, closed system thermochemical approaches to hydrogen release.
- The approach is novel and untried; it decouples the evolution of hydrogen from the formation of byproduct while greatly increasing the area available for reaction in both generating and receiving moieties. Of course, this approach will lower the mass percent by adding electrolyte but will have a minor impact on volumetric storage, so it could be useful for transport of hydrogen. Expanding the search to other systems of materials will help the chance of success. On the negative side, the team has yet to prove its conceptual model is correct. Until the researchers determine whether the liquid phase is merely a solvent increasing mass transport or an electrolyte facilitating ion transport, they cannot readily pick the right solvent and salts. Likewise, for the electrically assisted desorption, the team needs to verify whether it is indeed oxidizing BH_4 species and, thus, every hydrogen requires an electron, or if it is in some way catalyzing the production of hydrogen with less than one electron per BH_4.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team has completed a careful assessment of several materials against logical, well-justified criteria. Using literature thermodynamics data for hydrogen release and regeneration along with best estimates of kinetics from literature studies, the team has prioritized a number of candidates for further study. These materials have enough "head room" to add small quantities of low melting eutectics as solvent and still result in useful capacities. Armed with this list, the team is moving forward to assess these down-selected candidates in the presence and absence of added solvent. The quality of this work is demonstrated by a recent peer-reviewed publication of preliminary project results in the *Journal of Physical Chemistry C*. The team has made progress in performing additional studies on the hydrogenation of magnesium diboride, including MgB_2 with additives, or catalysts. The work has shown that, in the presence of a ternary iodide eutectic, MgB_2 with additives may be rehydrogenated to mixtures of magnesium borohydride and dodecaborane at reduced pressure of 700 bar versus 1.0 kbar in the absence of additives. Experiments are in progress to examine more carefully whether the quantity of the problematic thermodynamic trap, dodecaborane, can be minimized at lower temperatures and pressures. The team has fabricated and tested, in a proof-of-principle experiment, an electrochemical cell for the electrolysis of Li/K borohydride eutectic to produce hydrogen and some diborane from the electrochemical oxidation of borohydride. More details of how this approach to the onboard generation of hydrogen will have an impact on the overall onboard, closed system energy balance are hoped to be forthcoming.
- The assessment of electrolyte-assisted systems with 4 wt.% capacity appears to be very thorough and well done. Much consideration has gone into the analysis, providing a strong understanding of the systems. The

work related to reducing the pressure required for hydrogenation reactions is encouraging, especially since the principal investigator will be able to perform the testing in his own laboratory, thereby increasing throughput. The electrochemical work is interesting. Further work is required to understand the advantages of this storage method over conventional batteries.

- The researchers are making good progress. They have found, based on rational screening criteria, that several known systems could work well in this method. The team is following the test plan on lowering pressure and temperature in MgB system cycling. Furthermore, the team has developed apparatus for current testing.
- The research has shown nice results reporting rehydrogenation of MgB_2 in molten salts. The kinetics are still sluggish because the rehydrogenation takes 50 hours. Still, this points to promising rehydrogenation schemes that overcome diffusion limitations for ions.

Question 3: Collaboration and coordination

This project was rated **2.9** for its engagement with and coordination of project partners and interaction with other entities.

- The collaboration with Sandia National Laboratories (SNL) on the application of SNL's high-pressure hydrogen capabilities to the rehydrogenation of magnesium diboride has been effective and crucial to the team's success to date. Overall, the level of collaboration is commensurate with the budget and scope of the project.
- The collaboration between partners seems adequate, but there was not much collaboration outside the project.
- The project is a collaboration between California Institute of Technology, HRL Laboratories, LLC,, and Liox Power, Inc., with one Hydrogen Materials—Advanced Research Consortium (HyMARC) collaborator (Vitalie Stavila of SNL). The work would benefit from the characterization and computational tools available at other HyMARC partners.
- The team's collaboration with other HyMARC members could be improved. Though it is understood that this is a niche application for hydrogen storage, the utilization of HyMARC capabilities is highly encouraged.

Question 4: Relevance/potential impact

This project was rated **3.5** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This project has led to new ways of thinking about mass transfer diffusion limitation mitigation in systems with complex reactions (e.g., the Mg-B-H system). The use of low melting eutectics as solvents has led to significant increases in dehydrogenation and rehydrogenation reaction rates. This effort has led to progress against the difficult problems represented by the sluggish kinetics of hydrogen release and reuptake in the Mg-B-H system—perhaps more progress than any other project in the HyMARC sphere of internal projects and seedlings.
- This project is doing great work toward developing an understanding of the hydrogenation and dehydrogenation processes that are both severely limited on their own, as well as with electrolytes added to assist the reactions. If the reactions can be performed at considerably lower pressures and maintain their overall capacity, there could be significant impacts on storage space.
- Previously discarded systems can be taken and made viable by lowering pressure and temperature requirements and increasing kinetics. The project is well aligned with current Hydrogen and Fuel Cells Program goals.
- The use of molten salts to aid in ionic kinetics is a novel idea. Molten salts provide a wide parameter space for lowering the pressure and temperature for MgB_2 recharge.

Question 5: Proposed future work

This project was rated **2.9** for effective and logical planning.

- The proposed future work is encouraging, especially the improvements to MgB_2 uptake and the electrolyte-to-active-material ratio. The practical application of such a system is of great interest and will allow for the system tradeoffs to be identified. A practical application will also allow for a better range of material applications to be identified and test the suitability for vehicular applications.
- The team's future work follows logically from its preliminary work in Phase 1 and the subsequent period. The team continues to focus on the key problems that are inherent to employing additional mass to a material system while maximizing the benefits from the weight penalty of added solvent. In the project's future work on electrochemically driven hydrogen evolution from metal hydrides, it is suggested that the team provide a clear picture of how this will work in the vehicle system framework.
- The proposed future work is consistent with the outcomes.
- If the model is correct, the plan is viable. However, it is difficult to assess the validity of the model based on the data presented.

Project strengths:

- This project has a novel approach with the potential to change many aspects of the hydrogen charging and discharging process. The project team includes strong investigators with notable records of accomplishment. Since there are several chemical systems to pursue, there are many ways for the team to succeed.
- The team is excellent. The approach to developing low melting eutectics as solvents is well thought out. The team has developed well-considered selection criteria to determine which materials can best take advantage of the inclusion of a solvent to enhance the kinetics of hydrogen release/reuptake and have potentially practical applications.
- The project is very thorough. A great deal of attention has been paid to the details of this work, allowing for a strong understanding to be developed. Good progress has been made that enables future work, especially the reduced pressure operation of the reactions.
- Theoretically, the use of molten salts should work. These studies provide a wide parameter space (i.e., the molten salt and hydride system vary).

Project weaknesses:

- The project seems to have focused more on the assessment of materials rather than the empirical assessment of the materials, making the results look a little thin. It is important to understand which systems have the potential to work. Weeding out systems that are unlikely to work will hopefully speed experimental progress. The electrochemically driven system needs more justification; its advantages over other electrochemical systems are unclear. The plan to study materials at a practical level may be premature, as the performance at large quantities may not be understood sufficiently to make an accurate assessment.
- The team's commercial partner seems to be rather uninvolved. The team has not shown that the liquid is acting as an electrolyte. If the electrolytically assisted desorption works by BH_4 oxidation, then every electron made in the fuel cell will need to run through the storage system. This makes sense only if the voltage drop extracted is very small. Even if the investigators are correct, there are many parameters to consider, such as secondary (chemical) effects of electrolyte, possible catalysts, choice of base system, etc. Choosing the correct parameters is potentially a complex puzzle.
- The project lacks theory to guide the selection of additives (slide 11). Likewise, other factors should be considered. For example, the capillary forces between the particles that drive ionic motion (slide 2) could be important.
- The strategy of the electrolysis of metal hydrides to supersede thermochemically driven hydrogen release is unclear.

Recommendations for additions/deletions to project scope:

- First and foremost, the team should study the system in operando and verify the presence of the correct ions at the right concentration to be consistent with $Mg(BH_4)_2$ creation or desorption according to the project model. If the model is confirmed, the team should proceed. Otherwise, the team should regroup to determine the best solvent and salt if the liquid is a solvent, not an electrolyte. If this work has already been completed and was not presented, then there is no need to repeat it. The team should determine how many hydrogen molecules are produced per coulomb in the electrically assisted desorption of hydrogen. Unless there is far more than one hydrogen molecule for every two electrons, then the voltage should be measured or estimated. If there is found to be one electron per hydrogen molecule, as implied, and if the voltage is more than, say, 10% of the voltage in a single fuel cell plate, then the parasitic load is too high to be practical, and the electrically assisted work should be dropped. If the voltage drop is minimal or many hydrogen molecules are released with one electron, then the work should be continued. The team may consider removing material in various levels of hydrogenation and characterizing the particles to look for inhibiting layers or changes in morphology or other factors that might be stopping or greatly slowing uptake.
- A study of electrochemically driven hydrogen cycling compared to other electrochemical devices, such as batteries, should be done to identify the advantages (or disadvantages) of such a system. The team should focus especially on gravimetric efficiency and overall system efficiency when paired to a fuel cell. A practical study should be deferred until a better understanding has been gained and a more appropriate system demonstration has been performed.

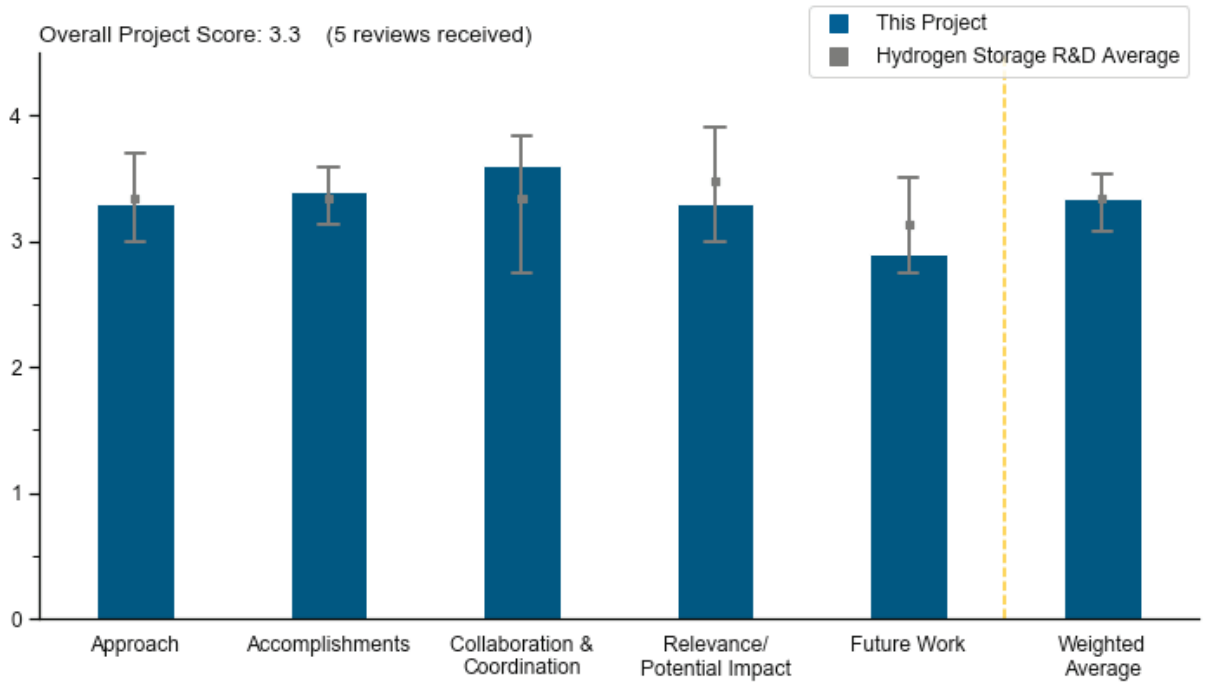
Project #ST-143: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Atomic Layer Deposition Synthesis of Novel Nanostructured Metal Borohydrides

Steven Christensen, National Renewable Energy Laboratory

Brief Summary of Project

Metal borohydrides (MBHs) such as $Mg(BH_4)_2$ possess high hydrogen storage capacity but insufficient charging/discharging rates and cyclability for U.S. Department of Energy targets. The project seeks to improve cycling/reversibility by increasing cycle life and to improve charging/discharging rates/kinetics. The project will achieve its objectives by incorporating a durable nanostructured phase and chemical additives that enhance reaction rates. The project team will use atomic layer deposition (ALD) to give the MBH a hard permeable coating to retain the nanostructured MBH phase for cyclability, as well as to catalyze the MBH using a thin layer of additives that enhance rates. The project addresses barriers associated with durability/operability, charging/discharging rates, and the lack of understanding of hydrogen chemisorption.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.3** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- This is an exciting approach: encapsulating metal hydrides within permeable oxide layers for the purpose of protecting the air-sensitive hydrides. Given the results of recent X-ray photoelectron spectroscopy (XPS) data regarding the structure of the surface of $NaAlH_4$ during dehydrogenation, Al-O-H phases are predicted to play a more significant role in the desorption process. It begs the question whether the alumina protective layers are also aiding in the surface rearrangement (by seeding Al-O regions) to aid in desorption.
- This seedling takes a different approach to nanoconfinement of complex metal hydrides, which is thought to enhance the kinetics of hydrogen release and/or alter the thermodynamics of multiphasic interactions in

the reacting material(s). The use of ALD to coat a complex metal hydride with an inert or possibly catalytic confining coating to enhance release and/or reversibility is an intriguing approach. Given that this is a seedling with limited funding and hence limited time, the scope of the approach is appropriate.

- The project approach is very strong and provides a solid foundation for investigating the coatings of MBHs. The use of ALD to coat the particles is clever, as is the methodology for understanding the mechanism for charging and discharging of the materials.
- The approach is interesting and innovative. It focuses on improving hydrogen sorption kinetics and cycling efficiency in nanostructured $Mg(BH_4)_2$ by using thin coatings formed by ALD to prevent particle agglomeration and serve as catalytic agents to enhance hydrogen sorption reaction rates and improve reversibility. ALD is a well-established technique for depositing thin films and coatings with single-atomic-layer precision. $Mg(BH_4)_2$ nanoparticles are provided by Sandia National Laboratories (SNL) as part of the Hydrogen Materials–Advanced Research Consortium (HyMARC) activity. That being stated, recent results, although provocative and potentially important, raise many questions that require detailed investigations that were not provided in the presentation.
- The concept of stabilizing the base material and doping it with a coating is good. However, using ALD raises cost concerns. Perhaps the same results could be achieved using another, higher-throughput method. The team has identified important barriers, and its work addresses these barriers.

Question 2: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Progress was made and clearly demonstrated in that the team improved the rate by using alumina coating and achieved even better success using titanium nitride. The team obtained a fortuitously good discharge result using boron nitride; however, boron nitride does not cycle. In contrast, the TiN coating might cycle. In total, over a dozen coatings were tried. Evidence suggests a surface contact effect. The team should be congratulated for acting on a serendipitous impact of BN coating. The team seems to be on track and may be verging on serious headway on the kinetics barrier, at least.
- This project has made great strides, especially with the development of the BN coated particles with a very good discharge performance. The particles themselves appear to have a good-looking structure and to be what the project seeks. The ability to get clean hydrogen out of the material at temperatures below 230°C is encouraging. If the material can cycle well (given that the mechanism is understood and the right kind of additives are used), considerations will need to be made to ensure the material does not go above 230°C and release products other than hydrogen. The ability to somewhat control the rate of reaction with additives in the coating is encouraging, as the current kinetics are very aggressive for fuel cell applications.
- The project seems to have managed to produce a surprising, but as yet unexplained, result: the rapid release (at 120°C) of hydrogen from nanoscaled magnesium borohydride upon which a BN or TiN coating has been applied using ALD techniques. This surprisingly facile release at a surprisingly low temperature of around 120°C is remarkable for a magnesium borohydride sample. It is heartening that this result has arisen from a fairly new seedling project. To explain this observation, significant questions must be addressed with experiments and characterization. Greater characterization of the nature of this material is important; however, the fact remains that a reasonable quantity of hydrogen is rapidly released by this material at a low temperature. Regardless of whether the process is reversible, the results have technological applications other than onboard vehicular storage.
- Nitride and oxide coatings have demonstrated enhanced desorption kinetics. The $TiN/Mg(BH_4)_2$ system shows good cyclability (slide 10). The BN with $Mg(BH_4)_2$ does not show as much cyclability.
- Modest progress was achieved using only an Al_2O_3 oxide coating on the nano-$Mg(BH_4)_2$. Compared to uncoated material, thicker oxide coatings produced improved H_2 desorption (approximately four times higher). However, when the team decided to forego the oxide layer and deposit a boron nitride "additive layer" directly onto the nanoparticles, a remarkable result was obtained. Heating of the nano-$Mg(BH_4)_2$ coated with a BN ALD layer to approximately 110°C produced extraordinarily rapid evolution of hydrogen. This was followed by evolution of other gas phase species (i.e., NH_3, H_2O, B_2H_6, and N_2) at higher temperatures. However, subsequent attempts at sorption cycling were not successful. This rapid dehydrogenation in the presence of the nitride coating is certainly provocative, but it raises numerous

questions. For example, it may be the case that the chemically aggressive precursor gases used to form the BN coating modify the composition of the nano-$Mg(BH_4)_2$ in some way that leads to a new species having a much higher dehydrogenation rate. It is certainly conceivable that in the presence of a highly reactive precursor gas, the very small (i.e., 50 nm diameter) $Mg(BH_4)_2$ particles could be consumed and converted to a different entity with entirely different hydrogen sorption rates. If that is not the case, the role of the thin BN overcoating in facilitating such rapid dehydrogenation from $Mg(BH_4)_2$ is unclear. If $Mg(BH_4)_2$ is indeed present, it is unclear why cycling was unsuccessful. Also, when a thin TiN layer is deposited on the nanoparticles prior to BN deposition, less H_2 is evolved, but the dehydrogenation temperature is still low. Similar questions need to be addressed in that case as well. In addition to the $Mg(BH_4)_2$ results, initial experiments using nano-Mg coated with BN and TiN also showed enhanced desorption rates. Overall, these are certainly intriguing results, but considerably more work must be done to elucidate the mechanisms, confirm the identity of the reactants, understand why cycling is limited, and validate the conclusions. In general, these issues were not discussed in the presentation.

Question 3: Collaboration and coordination

This project was rated **3.6** for its engagement with and coordination of project partners and interaction with other entities.

- Valuable collaborations with the HyMARC core team (on nanoparticle synthesis and material characterization), H2 Technology Consulting (on pressure–composition isotherm), and the Colorado School of Mines (on material characterization) have enabled the progress achieved thus far. Expertise and resources from cooperating organizations will undoubtedly be valuable in understanding results from the present experiments and in planning and conducting future work.
- There are a number of collaborations established with other researchers. These collaborations include the Colorado School of Mines, HyMARC partners at SNL, National Renewable Energy Laboratory (NREL), SLAC National Accelerator Laboratory, Lawrence Livermore National Laboratory, Pacific Northwest National Laboratory, and industry partner Forge Nano.
- The active collaborations with which the project is involved have been effective in the achievement of a remarkable result. The collaboration with HyMARC to obtain nanoscaled magnesium borohydride has been key to getting the project off the ground quickly. There should be some urgency in the team's future collaborations, and the team should focus on gaining spectroscopic information concerning the nature of the encapsulated material. The degree of collaboration appears commensurate with the scale of the project.
- The team has great collaborations with other partners and institutions. It makes great use of HyMARC resources, as well as those of outside organizations.
- The project demonstrates excellent collaboration, with real work being done by many players.

Question 4: Relevance/potential impact

This project was rated **3.3** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- While the project sought to explore another pathway to nanoencapsulation of magnesium borohydride, which was anticipated to be a complementary approach to either using porous material scaffolds or nanoscale graphene or related sheets, the project appears to have stumbled upon more interesting results. The rate of hydrogen release and the low temperature at which the release occurs suggests that this material is potentially interesting for applications in which reversibility is not a requirement. This material could thus have an outsized impact on solid-state storage for a variety of defense and national security applications, among others.
- The use of ceramic coatings as protective layers for hydrides is important. The reported data hints at the potential of these ceramic coatings to aid in desorption or uptake. If the coatings play a role in desorption or uptake of hydrogen, then it is crucial to determine this role using advanced characterization and careful design of experiments on coating/hydride pairs.

- This project aligns very well with the goals of HyMARC and DOE. The potential to develop a great storage material that challenges the current state of the art is very exciting and could have profound impacts on the hydrogen storage space.
- The desired impact, better kinetics and reversibility of $Mg(BH_4)_2$, would be game-changing. However, the cost of application remains a question. This project is aligned with DOE goals for storage.
- The project addresses problems that are central to the potential use of complex metal hydrides in practical hydrogen storage systems. Consequently, the project generally supports DOE research, development, and demonstration objectives. However, the provocative results raise numerous questions that must be addressed before the conclusions can be validated and the relevance and impact of the project can be firmly established.

Question 5: Proposed future work

This project was rated **2.9** for effective and logical planning.

- The proposed future work for the project will help identify the mechanism for charging and discharging of the coated materials and will help optimize the performance of the materials themselves. The future studies planned for the materials are on the right track to develop and increase understanding of related processes.
- The proposed future work is consistent with prior experimental results.
- Determining the mechanism is a key goal, which is excellent.
- The exploration of additives to achieve cycling is planned for next year.
- The team's proposed future work involves meeting one of the go/no-go decision points related to recyclability and determining the ALD-driven mechanism. It may be advisable, given the amount of funding, to prioritize the efforts and focus more on gaining information on the nature of the "encapsulated" material that gives rise to the rather remarkable hydrogen release rates at low temperatures. As the ALD process may give rise to doing chemistry between the substrate magnesium borohydride and the ALD reagent hydrazine, there needs to be some thorough spectroscopic characterization (infrared and nuclear magnetic resonance [NMR]) and elemental analysis to better define the nature of the material. This is likely of greater import than attempting to improve upon cyclability at this point in time.
- The recent results raise numerous questions and concerns that the NREL team should address (e.g., the composition of the nano-$Mg(BH_4)_2$ particles after BN exposure, the composition and microstructure after H_2 evolution, the failure to cycle). Although the NREL team is likely aware of these questions, none of the critical issues that should be addressed to support and confirm the conclusions are presented. The proposed future work in slide 15 is abbreviated and very general. Given the intriguing nature of the results, particularly the H_2 evolution rate, a more complete outline of proposed future work is needed.

Project strengths:

- This project has developed a very high-performance material that has encouraging potential for storage applications. Even if the material is not cyclable, if the cost is low enough, this material could push the state of the art. Furthermore, the project is structured very well. The group has an excellent and methodical approach to developing the materials and understanding how the materials work. The ongoing work has great potential to yield very fruitful results.
- The team members have obtained a surprising result, and the strength of the project now lies in this result. The onus is now on the team to explain the underlying chemistries responsible for this result. The decision to bring in an expert, Karl Gross, to validate the hydrogen release data is a strong choice.
- The strength of this project is in the potential for coatings to interact with hydrogen uptake and desorption rather than simply facilitate protection from oxidation. This aspect of the work deserves even more attention.
- This is an innovative project conducted by a well-qualified team. The results to date are intriguing and should stimulate interesting future work.
- The project concept is interesting. The team members have a good partnership and have obtained interesting early results.

Project weaknesses:

- The only project weakness is the investigators' choice to show the data on slides 9 and 10 prior to a verbal explanation by the presenter. There is beauty and elegance to representing many parameters on a single chart. However, these parameters require explanation. A slide explaining how these data should be read would have been useful. Such a slide is essential for reviewers who plan to read through the slides before the presentation date. It was only possible to understand and read these charts after being walked through the first one on slide 9.
- Given the observation of extremely rapid H_2 evolution from the BN-coated nano-$Mg(BH_4)_2$ particles at comparatively low temperatures, a variety of critical, detailed questions must be answered to elucidate the mechanism and support and validate the conclusions. These questions concern the possible reactions of precursor gases with the particles, changes in microstructure after evolution of gas phase products, reasons why the BN actually affects the H_2 evolution rate, and low cycling efficiency (among others). Special consideration must be given to understanding the composition and microstructure of the metal hydride nanoparticle after hydrogen liberation. None of these issues were addressed in the presentation. A candid examination of the results and a much more detailed plan for future research are needed.
- The application of a coating on the particles may make it difficult to understand exactly what is happening with the particles during cycling. Studies will have to be carefully designed to identify what is happening to the particles after discharge and charge when they are cycled to truly understand what the mechanism is and whether there is any way to improve the cycling of the material.
- Given that this is a seedling at a national laboratory, and the funding does not go very far, a potential weakness is the potential lack of funding to perform the needed characterization studies in detail. These studies are necessary for understanding how the ALD process has so significantly altered the chemistry of magnesium borohydride.
- It is necessary to better understand the commercial viability of the approach or alternate methods that might reasonably work if the project is to be technically successful. While battery particles are ALD coated, they are generally larger as well. It would be useful to perform a rough engineering calculation of the number of ALD machines needed to generate millions of tons of 10–50 nm particles.

Recommendations for additions/deletions to project scope:

- Spectroscopic characterization of the ALD-derived materials is recommended. Boron and nitrogen NMR is also recommended. Infrared spectroscopy will be useful in examining alterations in the B-H, N-H, and N-N bonding. The project should conduct elemental analysis of B, N, Cl, Ti, etc. It is recommended that a systematic series of ALD experiments be performed to explore what, if any, effect the order of addition has on the produced material's hydrogen release. Such experiments might entail comparing the currently practiced addition of hydrazine before BCl_3 with the addition of BCl_3 before hydrazine. Given the distinct possibility of a chemical reaction between hydrazine and magnesium borohydride, perhaps hydrazine should be deposited alone on magnesium borohydride. In the absence of magnesium borohydride, the ALD reactions may be performed on an inert substrate. Recyclability should be deprioritized until more is understood about the nature of the material that has been produced.
- If the material can be cycled to meet the targets, the mechanisms can be identified, and the material composition after ALD and cycling can be identified, it may be interesting to optimize the ALD coating thickness to reduce gravimetric and volumetric losses. However, this step is only recommended once a strong understanding of the material and its performance is developed.
- Investigators should perform a rough estimate of the cost to produce one million tons per year of ALD-coated particles of the size, thickness, and composition the team is using. At the very least, the amount of coating material needed per kilogram of particles should be determined.

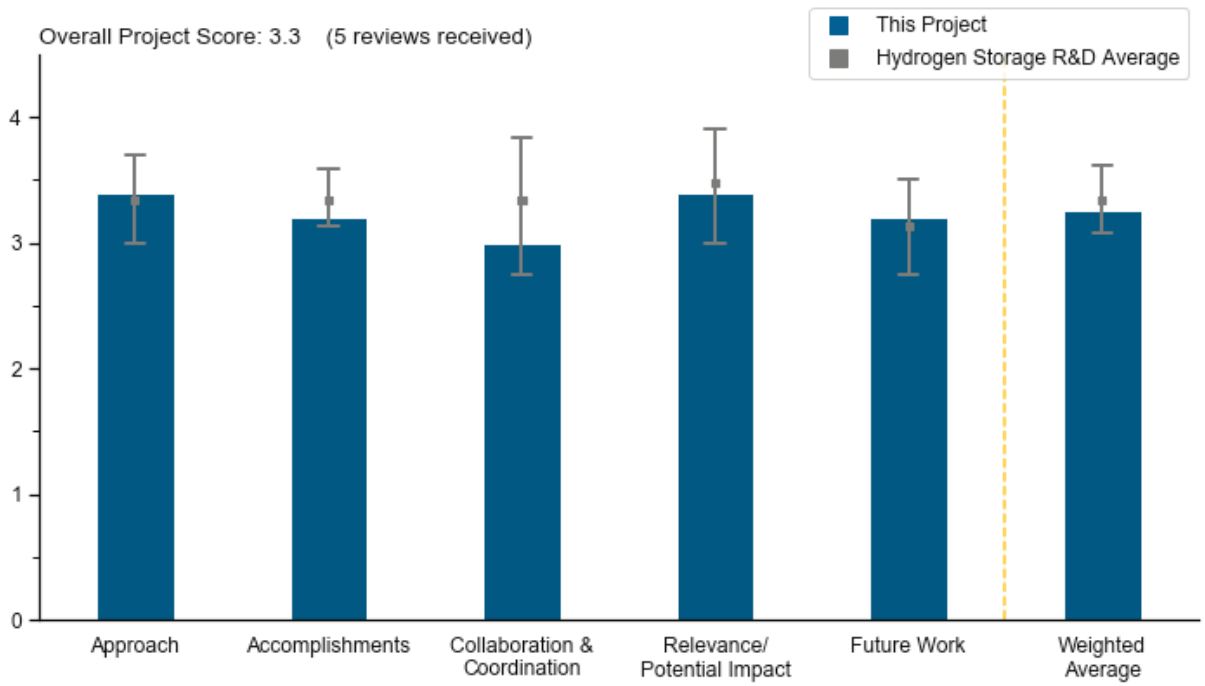
Project #ST-144: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Optimized Hydrogen Adsorbents via Machine Learning and Crystal Engineering

Don Siegel, University of Michigan

Brief Summary of Project

Screening of approximately 500,000 metal–organic frameworks (MOFs) revealed that essentially no compounds exceed 40 g/L usable capacity. New MOFs are needed to break through the volumetric ceiling. The project aims to develop purpose-built MOFs with high volumetric capacity, overcoming volumetric limitations associated with physisorptive hydrogen storage at both the materials and systems levels in MOFs. The project will apply machine-learning techniques to identify, design, and demonstrate high-capacity MOFs that demonstrate usable volumetric capacities exceeding 50 H_2 g/L (single-crystal/pressure swing) with no compromise to gravimetric capacity, kinetic performance, or reversibility. The project will also address packing inefficiencies, which can result in significant volumetric penalties in adsorptive hydrogen storage systems. Packing density will be increased at least 30% via crystal engineering, specifically control of MOF crystal morphology and crystallite size distribution. The project addresses barriers associated with volumetric density and gravimetric density.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- This project addresses two important aspects of the sorption of hydrogen on high-surface-area MOFs. The project approach is twofold. One task attempts to apply machine learning to screen, in silico, the many hundreds of thousands of MOF structure types, most of them not as yet synthesized, in the search for MOFs that can exceed what has been currently identified in the laboratory and hopefully exceed the technical targets for onboard storage. The second task is to explore crystal engineering approaches to significantly improve the packing density of microcrystalline MOFs, resulting in improved volumetric capacity for

hydrogen storage without decreasing the gravimetric capacity. The team has a very powerful approach to address the first task. This approach involves applying machine-learning computational tools to screen for high-capacity MOFs. This is a highly aggressive approach that is designed to utilize the high speed of computation. Machine learning is preferable to the very slow, mostly one-at-a-time attempted laboratory synthesis of all possible MOFs, currently a near-impossible task. The research has involved exploring the research team's previously developed database of nearly half a million MOF structures and applying a wide variety of machine-learning algorithms to explore the interconnectivity of a number of the key physical parameters that are likely involved in hydrogen sorption on the internal surfaces and volumes of the individual MOF structures. Such parameters include cavity diameter, pore diameter, surface area, density, pore volume, and void fraction. The team then ranked the algorithm's ability versus its own ability to predict the sorption properties of known benchmark MOFs. The "best" algorithm was then applied to the large database of structure types, and the gravimetric and volumetric capacities were computed for this huge set of MOFs, many of which are known but most of which are unknown (synthetically). This is truly an impressive feat. The attempted synthesis of a very small subset of structure types that appeared to have substantially higher performance than the benchmarks and the targets was then undertaken. The challenge to the approach then comes up against the need to rapidly attempt the synthesis of all of the promising "hits." The second approach aims to achieve higher volumetric capacities for sorbent materials. To this end, the project explores crystal engineering approaches to alter the shapes of the synthesized microcrystals to more symmetrical crystal shapes that have higher propensity to pack in dense three-dimensional arrays or alter the size distribution of microcrystallites to achieve higher overall packing densities. Both approaches, if successful, can enhance the overall volumetric capacity of a sorbent. This is also a very valid and focused approach to exploring the possibility of achieving enhanced volumetric storage capacity.

- The use of theoretical and other automated techniques is a valid and helpful approach to save time and resources relative to experiment only. The improved crystallite performance and improved packing are appropriate methods for achieving the goals. The use of machine learning on inputs to predict capacity and then reversing the model (using desired capacity to set the target zone of properties that will meet project goals) is an excellent idea. In the best case, this approach will be helpful, and in the worst case, this approach will confirm that we know most of what there is to know about what makes a good MOF. The risk in the approach is that there is no way to determine whether the selected MOF can actually be made, or will perform correctly. The hope, of course, is that the creation of the MOF will be successful and that it will perform as expected. Project barriers are clearly defined, and the project work is aimed toward surmounting them.
- The approach is focused on addressing the limitations of hydrogen storage volumetric capacity in MOFs. The strategy is reasonable and innovative; it involves control of MOF morphology and crystal size distribution to increase packing density and the use of machine learning techniques to identify candidate systems. Notably, the use of machine learning is a powerful and effective approach to extend predictive capabilities developed in prior work. The parameter space accessed in this study is huge. It provides researchers with a valuable baseline for initiating and benchmarking future work. However, the transition from identification of candidate MOFs using high-throughput machine learning screening to successful synthesis of the most attractive candidates remains problematic.
- The approach to the work is very thorough and does a great job of processing a very large amount of a data to separate out potentially interesting materials. The analytical methodology used is sound but could be improved by adding considerations for "synthesizability" that could improve the quality of the experimental results.
- This work focuses on computational and machine-learning approaches to selection of MOFs for maximum hydrogen uptake. As part of that objective, the work strives to close the gap between single-crystalline performance and powder performance (slide 5). A 500,000-item dataset was composed and analyzed for storage. Both pressure and temperature (together) and singular pressure were used as variables in assessing the MOFs.

Question 2: Accomplishments and progress

This project was rated **3.2** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team has made remarkable progress on the machine-learning approach to search for candidate MOFs that may have volumetric capacities that exceed the current benchmarks. The project has extended this year's approach to include temperature and pressure swing operation. The team has also performed further validation of the potential high-performing MOF structure types via more rigorous Grand Canonical Monte Carlo (GCMC) computational modeling. The outcome of this year's computational screening uncovered a large number of possible MOF candidates. The approach runs into the problem of then having to synthesize these structure types, many of them not previously synthesized, in the laboratory. The team chose to examine the top 10 candidates and attempt to synthesize them. The synthesis of the candidates is a laborious process that requires experimentation with many different conditions, solvents, and other parameters. Furthermore, many synthesis approaches may result in materials that are unstable or metastable upon removal of the solvent used in synthesis. This has been the case to this point, as two candidates resulted in apparent collapse of their porous structures upon solvent removal. More work needs to be done, but the team's effort is a very good one that will require patience. The crystal engineering effort shows promise. The team has demonstrated that control of the particle size distribution can lead to enhanced packing densities. The team's early efforts to control the morphology of microcrystalline habit shows promise, as the team has identified an additive that alters the morphology of MOF-5 crystallites to a variety of high-symmetry habits.
- A great deal of progress has been made in this work. The identification of MOFs that meet or surpass the targets is encouraging and will make experimental verification much simpler, as the number of materials is on the order of tens rather than hundreds. Though the results of the experimental work are encouraging, the work could be modified to include experimentation with different activation methods in an attempt to maximize measurable surface area. The results of the packing density work are very encouraging, especially with regard to the MOFs that have been synthesized with a higher packing density than previously seen.
- The team is making progress toward project milestones. The maximum error in prediction relative to GCMC calculation is about 1% and 5g/L and is less than one-third of that for most values, so the methods are consistent. Two of the high-capacity predicted MOFs were synthesized; however, neither had the properties desired. The project demonstrated that size control of particles can achieve enhanced system-level performance, which extended the range over which system performance is at particle performance levels. This is the main way in which measurable progress has been made toward DOE goals. To be clear, the theoretical side has made good progress in building tools, but the team has not had enough time to use them to find a winning MOF.
- The ability to predict the hydrogen storage properties for hundreds of thousands of MOF candidate materials is quite an accomplishment. Unfortunately, the "silver bullet" has not been found. Moreover, efforts to synthesize the best candidates from the machine-learning study have been largely unsuccessful. It is really quite amazing that MOF-5, among the first adsorbent systems studied, remains as one of the most promising candidates. The inability to synthesize a candidate that meets DOE targets notwithstanding, good progress was obtained in this seedling project. Methods for controlling MOF crystal morphology crystallite size distributions were developed. The machine-learning methods were optimized and validated to the extent that MOF compounds and associated adsorption properties could be predicted with confidence. All milestones through Quarter 7 of the project have been met.
- Most MOFs found using the machine-learning methods in this work are hypothetical. Therefore, variables related to processability should be used to optimize for yield in future computational work of this type.

Question 3: Collaboration and coordination

This project was rated **3.0** for its engagement with and coordination of project partners and interaction with other entities.

- The collaborators and the degree of collaboration exhibited by this project are appropriate to the size and scope of the effort. The team has utilized outside collaborators in key areas. Namely, the team has used systems models developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE) to provide guidance to its approach and, as needed, has collaborated with Ford Motor Company and University of Michigan faculty in materials synthesis and characterization efforts.
- Valuable collaborations within the University of Michigan and with the Ford Motor Company and HSECoE have accelerated project progress. The project is well managed and coordinated.
- The collaboration with other groups is good but could be strengthened by reaching out to other groups within and without HyMARC that have experience synthesizing MOFs. Such groups could provide feedback to maximize the value of the experimental testing.
- The team's collaboration between partners seems good and received some help from the HSECoE. However, there has not been much external collaboration so far.
- There were few collaborations outside of the University of Michigan and Ford Motor Company. Savannah River National Laboratory is listed as an unfunded collaborator.

Question 4: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This project is highly relevant in the search to break the "volumetric ceiling," a significant challenge in enhancing the volumetric capacities of sorbent systems. Success in this area will have a dramatic impact on achieving sorption materials that can meet or exceed the hydrogen capacity targets, which are significant barriers to practical application of sorption materials in engineered systems.
- Machine learning is a very useful technique for examining hydrogen sorbent materials. This work is extremely relevant to the field. However, it would be useful to quantify a "processability parameter" to decide on MOFs for inclusion.
- A system-level dense storage by adsorption would certainly be very useful. The general area (sorbents) has the best odds of success of the various methods outside physical containment, so progress in the area is relevant and aligned with DOE goals and targets.
- The work being done has the potential for great impact on cryogenic hydrogen storage materials. However, unless high uptake is shown at more useful (near-ambient) temperatures, the applications of this work will be limited to niche applications.
- The project is well aligned with DOE research, development, and demonstration objectives. This is a unique project in the Hydrogen and Fuel Cells Program (the Program) portfolio. The ability to computationally identify and benchmark thousands of MOFs for their potential as hydrogen storage candidates is valuable and has a positive impact on our understanding of hydrogen storage materials and development approaches. However, the fact remains that a superior candidate based upon the extensive machine-learning work has not yet been synthesized and tested.

Question 5: Proposed future work

This project was rated **3.2** for effective and logical planning.

- The proposed future work will help push the state of the art even further. The development of a high-capacity MOF would be a significant breakthrough. If performance is impressive enough to warrant further work, an increase in MOF tap density will be important for demonstrating the material's behavior in larger systems.
- Future work is tightly focused on achieving substantial improvements in volumetric capacity without sacrificing gravimetric capacity. The team's future work aims to break through the "volumetric capacity

ceiling" and remove the volumetric barrier in order to meet the technical targets for capacity in hydrogen sorbent materials.

- The project is scheduled to end December 31, 2020. The future work will focus on meeting the second go/no-go milestone: (a) identify an MOF with 10% increase over the current state of the art or (b) increase packing density by 15%. Ongoing synthesis work to produce a promising candidate selected from the results of the machine learning study is proposed. This synthesis work should be a research and development imperative for the remainder of the project.
- Given the team has two independent wings, the future work should include both milestone objectives (engineering and MOF selection). Both objectives are advantageous to this project and other related projects. However, since the decision to limit future work to one objective was approved, it is acceptable to focus on only one objective.
- The future work focuses on the second go/no-go milestone. The work will either focus on an MOF with a single-crystal volumetric capacity greater than 38 g/L usable capacity at 77 K or focus on a 15% increase in tap density through crystal engineering methods for a specific MOF compared to its non-optimized powder. It is unclear why there is an "or" statement (rather than an "and" statement). It is possible for the team of researchers to focus on both future work objectives.

Project strengths:

- This academic project is guided by industry. Though the project is led by theory, its results are experimentally confirmed. The project treats both engineering and material properties, giving it two ways to succeed and yield value. The team is excellent. The presentation was very well organized, easy to follow, and well constructed for the purpose of evaluating the work by Program Annual Merit Review metrics.
- The University of Michigan team is highly qualified and capable. This is an innovative project that provides DOE with an opportunity to explore a vast parameter space that has been too large and cumbersome to access experimentally. The project provides baseline and benchmarking data that is valuable to researchers investigating adsorbent systems for hydrogen storage.
- The project uses an aggressive approach backed by a knowledgeable, effective team. The approach of using machine-learning algorithms to enable high-speed screening of hundreds of thousands of compounds as sorption candidates contains many daunting challenges. This team is highly effective at addressing those challenges both in a computational sense and in an experimental sense. The team recognizes the need for accurate benchmarking of the computational results.
- The project has a very thorough and well-defined methodology that allows for fast identification of potentially high-performing materials. The ability to synthesize MOFs with a higher packing density than previously measured is a great step forward. The clever testing methods for packing density are commendable.
- Machine learning is an extremely valuable tool. Applying it to assessing MOFs for hydrogen capacity at pressure and temperature together and also only pressure swings is a good objective.

Project weaknesses:

- Synthesis of a few of the top 10 candidates represents a large potential bottleneck to future progress for this team. While the team appears to be very good at the synthesis of framework materials, perhaps the project could use some additional expert assistance or collaboration with the rather large-scope synthesis landscapes that may be required to successfully synthesize a few of the top 10 candidates that the machine learning approach identified. While this additional assistance is undoubtedly beyond the ability of the project to fund, the scope of the project suggests that this seedling needs its own seedling.
- Overall, it seems that the translation from a promising candidate identified from the high-throughput screening and machine-learning work into a real material synthesized in the laboratory has been largely unsuccessful. This is the most noteworthy project deficiency. It was unclear from the presentation why the synthesis of two promising candidate materials (MOF-31 and TMOF) failed to produce materials with significantly higher Brunauer–Emmett–Teller (BET) surface areas. It is also unclear whether any promising candidates with high surface area have been synthesized in this project. Perhaps additional synthesis collaborators should be brought into the project for the remainder of the activity.

- It would be beneficial to conduct an analysis of likely success rates from machine-learning prediction to experimental confirmation, based on predictions for MOFs with existing data (both good and bad MOFs).
- The experimental activation of the MOFs could potentially be improved by trying different methods to avoid pore clogging or collapse. There could also be a way to identify MOFs that are easier to synthesize than others to improve the quality of experimental results.
- Many of the highest-capacity MOFs (slide 26) were hypothetical.

Recommendations for additions/deletions to project scope:

- An investigation into an additional parameter that could identify how easily an MOF could be synthesized may be a worthwhile undertaking to improve the experimental results and increase throughput. This could potentially reduce the bottleneck of reviewing potential MOFs before synthesis.
- It would be useful to collaborate with experimentalists to determine processability of the hypothetical set of MOFs or to work within the confines of a series of MOFs that have been processed already.
- The project should be extended either to further examine machine-learning predictions of MOF stability or to determine the likelihood of possible synthesis for MOFs that pass the high-capacity screen. If likelihood of possible synthesis is determined, researchers can screen out MOFs with a lower likelihood.
- Additional attention to the attempted synthesis of the best candidates identified by the machine-learning approach is required. To thoroughly and successfully survey the usual synthetic parameters, the team may require additional staffing and funding.

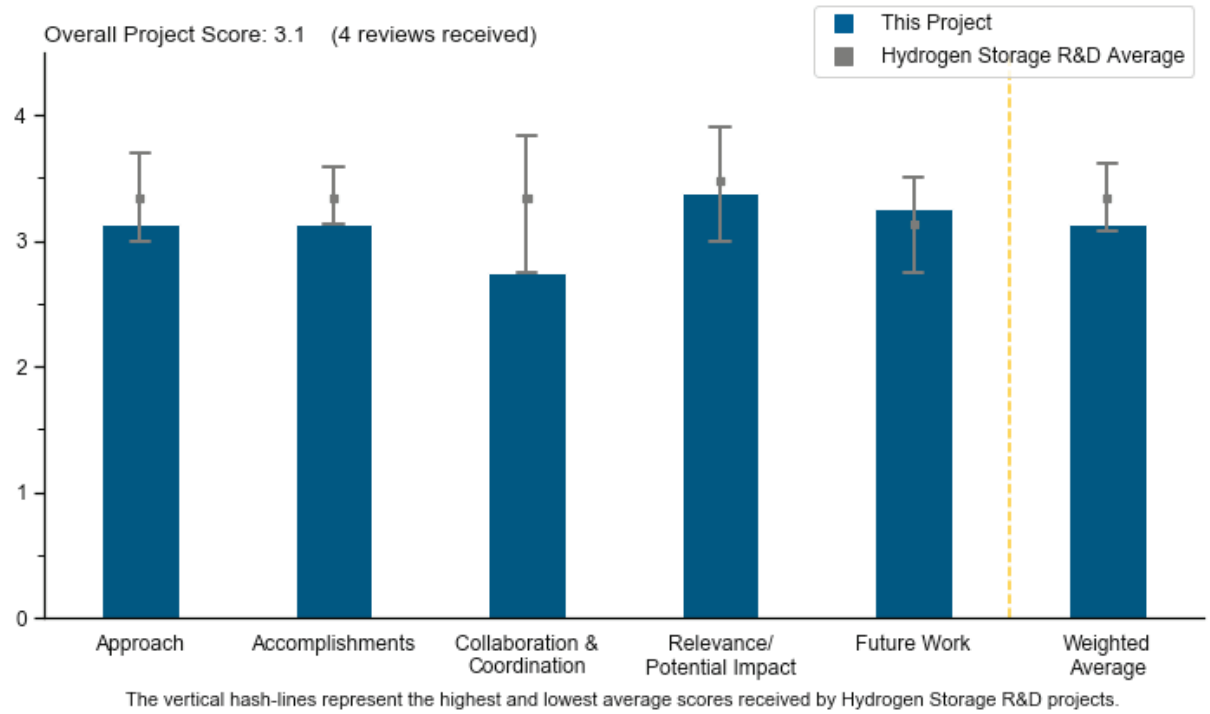
Project #ST-146: Precursor Processing Development for Low-Cost, High-Strength Carbon Fiber for Composite Overwrapped Pressure Vessel Applications

Matthew Weisenberger, University of Kentucky

Brief Summary of Project

This project aims to use low-cost carbon fiber precursor and develop a processing technology that can produce carbon fiber for hydrogen storage applications with tensile properties comparable to the current state-of-the-art at the U.S. Department of Energy target cost of $12.60 per kilogram or less. Cost savings are expected from several innovations: (1) use of non-exclusive, low-cost, high-quality polyacrylonitrile (PAN) known as Tech-PAN polymer as precursor instead of a proprietary PAN polymer, (2) use of hollow carbon fibers that enable up to 35 times faster oxidization and carbonization than existing processes, and (3) water use reduction and solvent recovery using activated carbon. These process improvements in carbon fiber production have the greatest impact on product cost.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.1** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach focuses on four cost drivers to reduce the cost of T700S-equivalent fiber toward a target of $10.68/kg, which is below the U.S. Department of Energy goal of $12.60/kg. The demonstration using TechPAN appears to be validated in that carbon fibers were produced in the laboratory with over 10% exceeding T700S average tensile strength. Carbon fiber made using TechPAN is expected to result in 13.8% cost reduction, and as an open-source PAN, it offers a path forward toward commercialization and innovation. Better utilization of PAN using the hollow-fiber approach, eliminating the poor quality core, has some validation based on the literature and should result in net cost reduction. The faster oxidation rate of 35x seems unlikely, in that oxidation in a continuous fiber is unlikely to occur from the center, but for a thinner-wall fiber, it will still be faster than a solid fiber.

- The approach is strong. It is difficult to improve an approach that could reduce carbon fiber cost from $29.40/kg to $10.68/kg.
- The hollow-fiber approach is novel and could offer additional cost savings. It is not clear if all of the cost savings are being realized. For example, the fiber-mass-per-foot would be lower for the hollow fiber relative to the solid fiber, thereby providing more material for additional fiber length. It would also be prudent to discuss defect challenges that need to be overcome in increasing fiber strength and modulus. The presentation did discuss hollow-wall collapsing, which the project demonstrated did not happen, but it is unknown whether there are other issues that have been identified that need to be addressed as well.
- The project was able to produce hollow fibers. The presenter did not give an adequate response to how oxidation would be reduced from over an hour to 10 minutes. Assumptions were made that the process would occur faster because of stabilization occurring both from inside the hollow fiber and outside the fiber. There was no clear approach to reaching this goal. The economic analysis lacked important details. It showed percentage improvements that somehow got to $10.68/kg cost for carbon fiber. This was not supported in the presentation other than slide 6 indicating how one could get to $23.82/kg. No estimate was provided on how improved specific properties and increased oxidation would result in an additional $13.14 in savings. The solvent recovery using activated carbon should be a separate project, given the challenges of winding, oxidizing, and utilizing hollow fibers.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project has made strong progress to date. (1) Fiber was spun with the TechPAN, and initial properties showed the potential to meet or exceed T700S strength. (2) Hollow fiber was spun using a scalable approach; there may be some possibility of refining the approach by shaping the die, but for now, at least, hollow fiber has been spun. (3) Initial feasibility of solvent recovery has been demonstrated using activated carbon. (4) The oxidation rate should be evaluated soon to get a better estimate of kinetics via a small-fiber sample in thermal gravimetric analysis (TGA). The effect of wall thickness to fiber diameter as it relates to oxidation rate and morphology needs to be evaluated before scale-up. (5) The effect of using hollow fiber, and hence the expected reduced composite fiber volume, should be discussed with compressed gas system (CGS) tank manufacturers to forestall unexpected consequences, such as thicker shell-wall requirements.
- The project has clearly defined goals, and the presenter showed the approach and how the project was going to partly lower the cost. An area of improvement would be to demonstrate how the cost is going to be reduced even further. It would be beneficial to know if the research team has ideas about how they are going to move beyond the current savings they believe they can achieve. The first data sets for the fiber properties are okay. They do fall short of the T700S target, but they are pretty good. The one challenge the team will need to overcome for the pressure vessel fiber use is the low coefficient of variation (CV). The pressure vessels will design to the lower part of the CV, which will increase weight, volume, and cost. The strength goal is important, but the CV is just as important. The current data set has a lot of variation. It is unclear whether a calculation has been performed on the stress of the hollow cross section or whether it is based on the fiber diameter itself. How the strength was determined was not clear in the presentation.
- Fibers with strength similar to T700S were made and solvent recovery was successful, resulting in some cost reduction.
- The presentation lacked consistency. Slide 22 indicates that filaments of ~100 um were produced, with a pathway to reaching ~14 um to be determined. Slide 18 states that fiber of ~150 um was successfully spun. Slide 11 indicates that 76 um was achieved. If this is correct, then the project has already reached the year 2 go/no-go milestone. The project team has also claimed that the project met the $23.82/kg fiscal year (FY) 2019 go/no-go. Part of that was attributed to TechPAN, which is not part of the project development but a separate proprietary development of the University of Kentucky (UK). The project's progress seems limited on avoiding collapse of fibers during spinning and oxidation rate.

Question 3: Collaboration and coordination

This project was rated **2.8** for its engagement with and coordination of project partners and interaction with other entities.

- The UK Center for Applied Energy Research is collaborating with Oak Ridge National Laboratory (ORNL) via funding under the Lightweight Materials Consortium (LightMAT) in carbonization. There was some discussion whereby UK could spin fiber from the other two programs. As the project proceeds toward validation of the cost-saving concepts, it is suggested that the project team engage in discussions with a CGS tank manufacturer to learn of any concerns or suggestions regarding handling characteristics or properties of a new fiber.
- It was clear on the collaboration efforts between ORNL and UK where they were contributing. It would be beneficial to have a tank manufacturer as part of the advisory team to provide relative design feedback required by the fibers, such as the CV.
- The collaboration with ORNL seems to be working well and providing good value to the project. There may be additional collaborations within the Hydrogen Materials Advanced Research Consortium (HyMARC) that could be leveraged for this project.
- The project's collaborators have no commercial interests. The role of ORNL was not clearly defined, other than scale-up. This reviewer is not familiar with the separate LightMAT objectives, so there may be an insufficient basis to rate this criterion.

Question 4: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- The project has the potential to significantly reduce the cost of high-strength carbon fiber for use in CGS tanks. The project begins with a basic cost model, which is useful for tracking progress regarding cost reduction in each of the four areas. The project has potential synergy with the other carbon fiber projects. If the hollow fiber concept meets expectations, it might be applied to the other precursors under development. The use of activated carbon to capture solvent also may be applied to other PAN precursors. Follow-up research will be required to understand any issues regarding the use of hollow fiber versus conventional fiber. Low-cost, high-strength carbon fiber is expected to have broad applications as a structural material.
- This project is extremely relevant and its potential impact would be advantageous to meeting DOE's targets and to the industry.
- It is well known that compressed hydrogen technology cannot meet all of the DOE targets, so a project focused on this technology could not be said to significantly advance toward the DOE project goals and objectives. However, this project does align with the Hydrogen and Fuel Cells Program objectives and has the potential to advance progress toward DOE goals. Of all of the projects, this is the most likely to have impact on the industry in the near term.
- The project aligns with system weight and cost objectives.

Question 5: Proposed future work

This project was rated **3.3** for effective and logical planning.

- The project's milestones and go/no-go's are appropriate and at a high level, regarding meeting tensile strength targets of 4.9 GPa. Details regarding the experiments and approach to meeting these goals were not presented. Data tables and/or charts of the kinetics of oxidation, microstructure, and carbon fiber properties should be prepared as a function of fiber diameter and wall thickness to help establish a basis for future process optimization.
- The project team's proposed future work discusses more on fiber-spinning development and cost reduction processes, but the team needs to be focused on increasing the fiber strength and reducing the CV after reducing the fiber diameter. Cost reductions in the wastewater will be irrelevant if the fiber performance cannot be achieved.

- The project team provided the planned milestones for FY 2020 and barriers to be addressed. The team should not wait until the end of the project for cost evaluation; there should be a preliminary estimate for all cost factors by end of FY 2019.
- The project's remaining tasks are a logical continuation of the work done so far and will focus on all three critical barriers.

Project strengths:

- The project explores the following potential technologies, which individually provide value for meeting DOE goals. (1) TechPAN may serve as a low-cost, commercial, open-source model precursor for future fiber development work. (2) The concept of hollow-core fiber may transition to other fiber precursors; the effect of process conditions on morphology and properties needs deeper study and perhaps modeling.
(3) The recovery of process solvent has the potential to save energy, water usage, and cost.
(4) Micromechanics analysis of carbon fiber surface area to fiber cross-section should show benefit in stress transfer across the matrix and throughout the composite. Detailed analysis should be used to help establish optimized geometry.
- The project's strengths include a novel approach in making hollow carbon fibers. The work in cost reductions can benefit DOE's targets, and the goal to achieve strength parity with T700S is a good target.
- The project's strengths include the team's facilities and that it has achieved a measure of success in producing hollow fibers.
- The overall project methodology and approach are strong. There are clear milestones and a clear outline of the progression of the project. The results are clearly presented.

Project weaknesses:

- The project is focused on the fiber spinning, which is important, but there seems to be less discussion or emphasis on the approach to achieve the high performance of the hollow fiber. With a hollow-fiber design, the wall stress will be higher in tension, with a reduced cross-sectional area. A simple calculation comparing the solid-fiber strength average to the theoretical hollow-wall strength average should be considered to demonstrate what level of fiber quality will need to be achieved. Another item not addressed is the fiber wall buckling or collapsing on bending. The solid core, even without the additional strength proved in tensile, does keep the fiber wall from collapsing inward, thereby minimizing additional stresses.
- A majority of the expected fiber cost savings is based on a much higher oxidation rate of 35x. This higher rate includes an assumption that oxidation could occur from inside the core. It is unlikely oxygen can penetrate into the core unless fiber defects exist that allow for oxygen transport. Regardless, a shorter distance for diffusion, assuming a thinner wall, will allow for less time to oxidize the fiber. If an oxygen-carrier gas or liquid is included in the core during spinning, it may be possible to accelerate oxidation, but this would add to the complexity.
- There is a lack of clear direction to solving critical problems, at least as described in the presentation and question-and-answer segment. The project's other weaknesses include a reliance on a non-commercial grade of precursor, the lack of industrial participation, assumptions on oxidation rate and ability to achieve diameter and spinnability, and reliance on tensile properties. Although this is correctly focused on the gas storage application, something should have been mentioned about suitability of hollow fibers for other applications.
- The whole project hinges on the assumption in slide 10 that hollow fibers could be as strong as solid fibers because the core section does not significantly take on a tensile load. Some quantitative analysis would have been useful to show that this could be the case, although on slide 22, the principal investigators state this is beyond the scope of this project.

Recommendations for additions/deletions to project scope:

- Two additions to the scope could be recommended. One is analysis of critical assumption number three ("the sheath of the carbon fiber carries the majority of the force when in tension, and therefore hollow carbon fibers should provide the same tensile strength performance as conventional solid carbon fibers"). The second would be an analysis of the effect of using a hollow fiber in a composite pressure vessel. There

are questions to be investigated, such as whether load transferred between carbon fiber layers is the same as with solid fibers, whether the fiber will remain a hollow cylinder or flatten out when under tension while wrapped around a cylinder, and whether it will flatten during winding. This could be an opportunity to collaborate with some of the modeling capabilities within HyMARC and so would not necessarily be an additional workload for the principal investigators.

- The project as proposed is on the right track. Future results may drive changes, but at this stage, it is too early. The project team should make sure that data collection allows for scientific understanding relating to the processing of hollow carbon fiber, particularly relating to kinetics and morphology as it relates to fiber diameter and wall thickness.
- The project team should delete the activated carbon for solvent-capture work and focus on the fiber challenges.

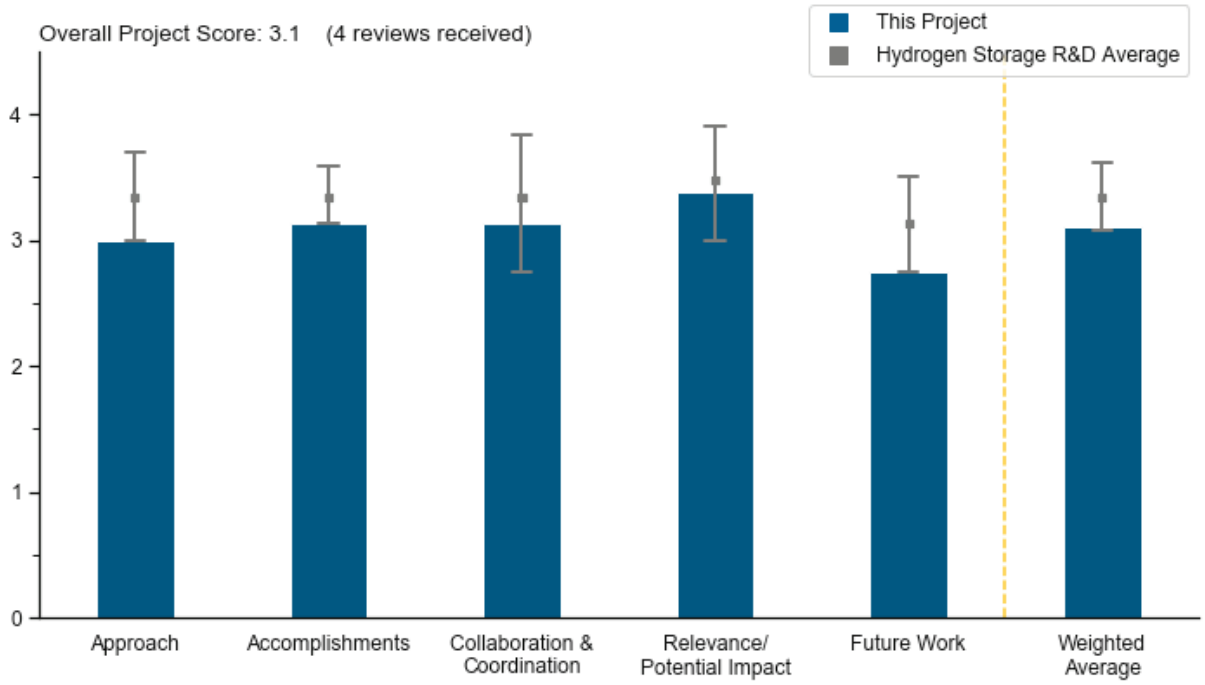
Project #ST-147: Developing a New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber

Mike Chung, Pennsylvania State University

Brief Summary of Project

This project seeks to identify new potential low-cost alternatives to polyacrylonitrile (PAN) to be used as a precursor in the manufacture of high-strength carbon fiber. A systemic study will be conducted to identify several new hydrocarbon polymer precursors that can offer greater than 80% yield in a one-step carbonization process under nitrogen atmosphere. Use of a new class of polyethylene (PE)-co-pitch polymer precursors and boron-containing pitch precursors will also be investigated. The most promising precursors will be selected for further development and analysis.

Project Scoring



The vertical hash-lines represent the highest and lowest average scores received by Hydrogen Storage R&D projects.

Question 1: Approach to performing the work

This project was rated **3.0** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The approach to producing low-weight carbon fiber precursors by looking at alternatives to PAN is well-thought-out and presented. It is clear that the cost will be reduced by using a less expensive precursor. However, it is not clear from the presentation how this project is tackling the system weight and volume and suitable hydrogen-binding energy barriers.
- The project's approach is a serious attempt to change how carbon fiber is manufactured, using a pure hydrocarbon polymer that is melt-processable and provides high carbon yield in one-step carbonization. One downside is that the presentation provided support for chemistry and some processing but little information on what was actually achieved versus metrics and milestones.
- The approach is high-risk and yet high-payoff. The polyolefin precursors are developmental at small scale; however, they do use commercial feedstocks, and the synthesis has a high yield. The precursor has the potential to have low cost and very high conversion yield to carbon fiber. The carbon fiber does not require

oxygen stabilization, which should also save cost. It would be beneficial to see a basic cost model developed for this approach as the technology matures.
- The approach to melt-spinnable PE fiber with C content is demonstrated as possible; however, the fiber quality is lacking significant defect-free surface and core in the fiber. As shown, the current approach in increasing the carbon content and stabilizing through cross-linking will be irrelevant if the fiber spinning quality cannot be met. There will be no advantage or improvements in fiber strength.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project has done an excellent job of evaluating a number of approaches to achieving a precursor with high char yield that is spinnable into a fiber. The first fibers spun appear to have many defects and would have low tensile strength. The precursors could establish a new paradigm for carbon fiber; however, it will be very important to demonstrate the ability to achieve high strength. A basic cost model should be established at this point in the project.
- Polyolefin precursors have been melt-spun and carbonized, and good mass-loss characteristics have been observed. The project is well on its way to meeting the next set of milestones. There is some concern about the roughness seen in the scanning electron microscope (SEM) pictures on page 15, compared to that of T700 (see figure 7e in http://dx.doi.org/10.5714/CL.2016.18.018); there is also concern that, although the fiber may cost less, the fiber is going to be much weaker.
- A new class of polymer precursors has been developed, and another has shown high conversion yield. The presentation lacked information on economics and was not clear about what precursor will be down-selected and scaled up in the remaining fiscal year (FY) 2019 work. It appears that improvement in fiber morphology may be needed, as indicated in results from Oak Ridge National Laboratory (ORNL).
- Based on the current status of the project, the strength performance needed for DOE goals will not be met. The cost may be reduced, but it does not matter unless the fiber strength requirements are met.

Question 3: Collaboration and coordination

This project was rated **3.1** for its engagement with and coordination of project partners and interaction with other entities.

- Based on the information here, the collaborations with ORNL and within The Pennsylvania State University seem to be working well and providing good value to the project. Results from the ORNL team are also presented. There may be additional collaborations within the Hydrogen Materials Advanced Research Consortium (HyMARC) that could be leveraged for this project.
- The project team is fortunate to have ORNL helping spin and convert fibers. There should be more interaction to help improve the fiber-spinning quality and fiber performance measurements after conversion.
- The project's collaborators include the Lightweight Materials Consortium (LightMAT), with ORNL to spin the fiber and convert to carbon. This level of collaboration should be sufficient to meet the project goals.
- It would be helpful to have a better understanding of how LightMAT's funding of ORNL supports work directly related to this project. There is no independent assessment or report seen from ORNL.

Question 4: Relevance/potential impact

This project was rated **3.4** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- The project could have a very significant impact if the ultimate carbon fiber has the required mechanical properties. The starting materials should have much lower cost than current PAN, and the simpler and faster processing into carbon fiber should be much cheaper. It will not be possible to fully explore and

optimize the best precursor and processing approach under this current project; rather, it is important to show the potential of the technology to produce high-strength carbon fiber.
- The goal of reducing the cost of carbon fiber is well within the relevance and potential impact to help DOE reduce pressure-vessel costs.
- If successful, the project could have significant technical achievement.
- It is well known that compressed hydrogen technology cannot meet all of the DOE targets, so a project focused on this technology could not be said to significantly advance toward the DOE project goals and objectives. However, this project does align with the Hydrogen and Fuel Cells Program's objectives and has the potential to advance progress toward DOE goals.

Question 5: Proposed future work

This project was rated **2.8** for effective and logical planning.

- The proposed future work discusses continued work on the melt-spinning PE, with various x-link and B pitch materials. This may be appropriate for investigating the quality change in the fiber and the direction of adding the downstream process of the spinneret with heating and tensioning for better molecular alignment. However, the surface quality and fiber porosity need to be critically addressed, and it is hoped that this is the intention for the future work that is planned.
- The most critical step of developing and producing fiber from a new polyolefin precursor has been met. Future work needs to focus on producing better-quality carbon fiber with a baseline precursor and then perhaps modifying the precursor to make carbon fiber of even better quality. A basic cost model should be developed, and metrics should be captured during the remaining project.
- The future work is in line with the milestones and project goals. However, as in the approach, it is unclear how suitable hydrogen-binding energy is being addressed.
- The linkage of the milestone summary table to the few slides on summary of future work was unclear; it was hard to tell if this was remaining FY 2019 or FY 2020 work.

Project strengths:

- The project is well planned, and it is clear that the principal investigator is a leading expert in polymer chemistry. It is appreciated that, although there was a good deal of chemistry in this project, it was presented in a way that could be easily understood by a physicist. The systematic approach and analysis make the project valuable to DOE.
- The project's strengths include the development of new pitch precursors and a possible one-step carbonization process.
- The team did a thorough job of developing and evaluating a number of new polyolefins, which may provide high-strength carbon fiber as well as other important applications.
- The project's strength is the reduced costs of fiber spinning and precursor materials.

Project weaknesses:

- The project is laser-focused on the materials aspect, which is both a good and bad thing. Because of that, it is not always clear how the research is addressing the barriers seen on slide 2. For instance, it is clear that the cost is being addressed in a general way and high polymer surface area is addressed through the chemistry, but these are the only barriers that appear to be directly addressed. This is likely partially due to the scope of the project and the way the milestones are defined.
- While it is still early in the project, the initial fiber spun from the precursor was of poor quality. Further work needs to be done quickly to validate that high-quality fiber can be produced from this new class of precursors. A cost model needs to be developed, perhaps in collaboration with ORNL.
- There is no clear path described on how the project team will increase fiber quality to meet the strength requirements for the low-cost, high-strength fiber.
- There is a lack of standard project management reporting.

Recommendations for additions/deletions to project scope:

- The project has potential for high payoff; however, given the amount of effort required to develop and characterize the new precursors, the project is underfunded. More effort needs to be applied toward ORNL to spin high-quality fiber.
- Although this is definitely a materials research project, it would be interesting to see some estimation of the cost savings for using polyolefin precursors over traditional PAN. Otherwise, no change to the scope is recommended.
- The project team should focus on improving fiber quality.

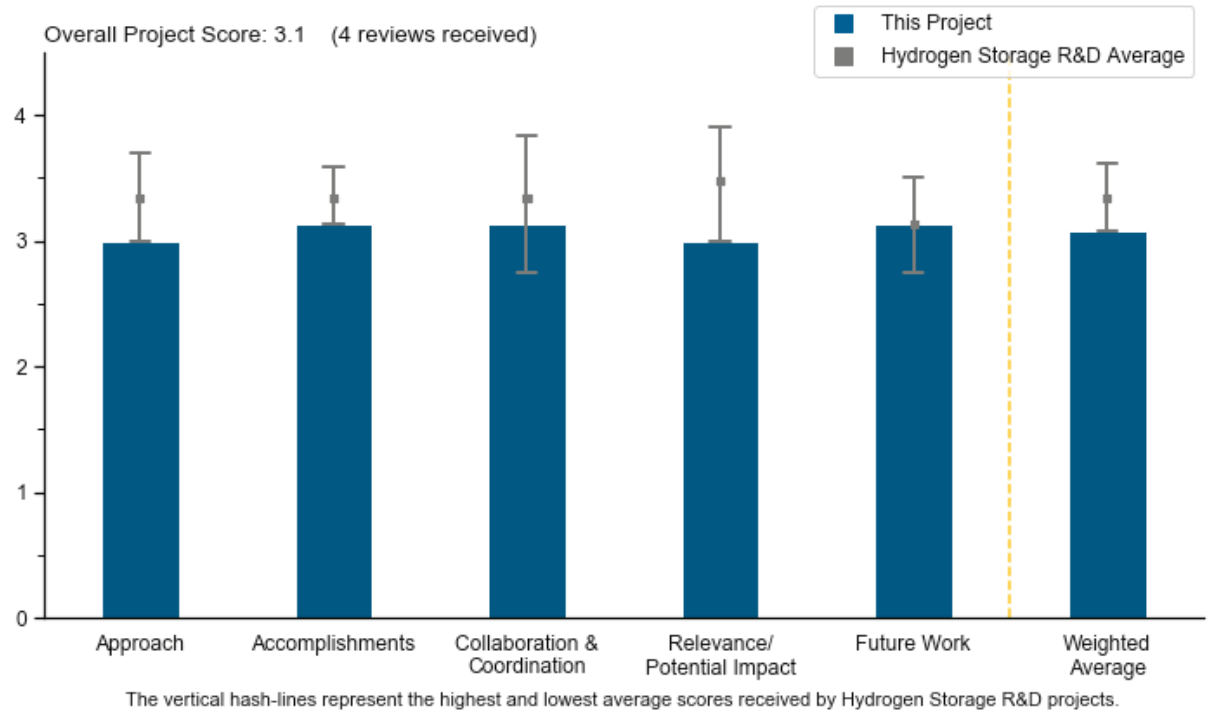
Project #ST-148: Novel Plasticized Melt-Spinning Process of Polyacrylonitrile Fibers Based on Task-Specific Ionic Liquids

Sheng Dai, Oak Ridge National Laboratory

Brief Summary of Project

The goal of this project is to develop a novel plasticized melt-spinning process based on nonvolatile task-specific ionic liquids (ILs) to replace the current solution spinning process. The four main research tasks are (1) investigation of how the molecular structures of ILs dictate plasticizing interactions with polyacrylonitrile (PAN), (2) study of how the chemical interactions of ILs with PAN can be used to control the cyclization degree in intermediate ladder structures, (3) integration of the information gained from the first two tasks to develop IL-assisted melt-spinning systems, and (4) demonstration of considerably enhanced production efficiency of PAN fibers. If successful, the developed technology is expected to result in significant cost reduction for carbon fiber.

Project Scoring



Question 1: Approach to performing the work

This project was rated **3.0** for identifying and addressing barriers, project design, feasibility, and integration with other relevant efforts.

- The use of ILs in a melt-spinning process appears innovative and has been shown to reduce melt temperatures of commercial-grade PAN. An issue with the work scope is that this project, although needed and useful, may not be the most critical link in developing cost-effective carbon fiber for hydrogen storage applications. The effort devoted to understanding the stabilization process for PAN fibers is questioned. This is a well-known, or at least well-practiced, process, and Oak Ridge National Laboratory (ORNL) should already have a good understanding of this process. The morphology of the fiber-drawn PAN fiber precursor appears to be excellent.
- The novel approach is an excellent idea to improve the processability of the PAN precursor and understand the effects of the IL on the fiber properties. Being able to melt-spin PAN would be a benefit, lowering the processing costs to be similar to gel spinning. The approach is very logical and appears to be well executed.

- The approach to producing a new melt-spinning process for PAN using ionic liquids is unique and fits well into the U.S. Department of Energy project portfolio. It is stated that the cost will be reduced by using this process, although a technoeconomic analysis is yet to be completed. However, it is not clear from this presentation how the project is tackling the system weight and volume barrier.
- The approach is to reduce the cost of spinning PAN into fiber by using melt spinning through addition of ILs for plasticization. It is not apparent that this approach will reduce the cost of the carbon fiber; it could make it more expensive. The ILs are relatively expensive and may be recovered for reuse through fiber-washing. Since the fiber must be washed after melt spinning, it is not apparent that this is any better than wet spinning. The project requires a cost model to validate the potential for cost savings. It is not clear at this time whether the IL could result in weaker or stronger carbon fiber.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The author demonstrated >15°C decrease in PAN melt temperature (later stated to be >100°C reduction) and good spin morphology and is processing a commercial range of fiber diameter. A patent for the process is being prepared. Carbon yield greater than 50% was achieved. More progress on the technoeconomic analysis was expected, but the analysis should be ready by the end of FY 2019. The 525 Solutions Inc. analysis of IL costs in the context of the presentation listed a cost advantage that was not converted into process-cost benefit.
- The project is progressing very well and has demonstrated progress on investigating fiber morphology. The fiber surface and core quality will directly affect the carbon fiber properties that will inhibit the fiber property performance. The project has demonstrated the ability to make good-looking, quality fiber that will help toward the project's and DOE's goal of reducing cost with high-performance fibers.
- The progress toward meeting the project objective is good. The solubility and resulting rheology changes made it possible to melt-spin PAN fiber. Washing the fiber showed it may be possible to recover 80% of the IL. It is not clear how any residual IL in the carbon fiber might affect its mechanical properties. While a cost model is being developed to determine the cost of the IL, there needs to be a focus on cost for the new carbon fiber.
- PAN melt temperature has been reduced by an order of magnitude past the milestone goal. The project is well on its way to meeting the next set of milestones. It is unclear how the system weight and volume barriers are being addressed. For the technoeconomic analysis, only the cost of the IL is estimated. It is unclear (quantitatively) whether the overall cost will be reduced. Additionally, from an original equipment manufacturer perspective, these ILs would not be considered a capital expenditure.

Question 3: Collaboration and coordination

This project was rated **3.1** for its engagement with and coordination of project partners and interaction with other entities.

- Based on the success of the project, the team appears to be well coordinated. In subsequent reviews, it would help to identify during the presentation, and in the presentation, what part of the work was done with the collaborators.
- ORNL's role was not described in sufficient detail. This project could have the best potential for technology transfer in the near future. It would be helpful to establish a metric from some type of industrial participation before the end of the project.
- There is some collaboration with an IL supplier for technoeconomic analysis. It is unclear if this is really an effective collaboration. Cost analysis of the IL is not sufficient to show whether there are any cost savings over fibers made from traditional PAN. The collaborations within ORNL appear to add good value to the project, though.
- 525 Solutions Inc. is under subcontract to develop technoeconomic analysis and scale-up for IL.

Question 4: Relevance/potential impact

This project was rated **3.0** for supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan.

- This project is very relevant to DOE goals and has the potential to have impact on the cost and performance of the carbon fibers related to pressure vessels.
- This project is an incremental but necessary area of improvement for the melt spinning of commercial PAN fibers and associated processing and environmental improvements.
- It is well known that compressed hydrogen technology cannot meet all of the DOE targets, so a project focused on this technology could not be said to significantly advance toward the DOE project goals and objectives. However, this project does align with the Hydrogen and Fuel Cells Program objectives and has the potential to advance progress toward the DOE goals.
- It is too early to determine whether the approach has a pathway to reduce carbon fiber cost. It is also too early to know what type of carbon fiber may be generated using this technology and whether the IL approach will help or hinder the performance.

Question 5: Proposed future work

This project was rated **3.1** for effective and logical planning.

- The future work plans appear adequate for the current stage of the effort: developing a better understanding of IL variants and effects on PAN rheology. The project needs some focus on a comprehensive cost model. The project also needs to validate that residual IL will not disrupt carbon fiber morphology, leading to weaker fiber.
- The project's future work aligns with the overall project objectives. It is, however, still unclear how system weight and volume are affected, and the technoeconomic analysis of the IL by itself seems to add little value to the DOE portfolio.
- The future milestones, future work, and current stage of the project were clearly defined. The possible use of TechPAN is questionable without a clear supply route defined.
- The proposed future work is on target for what needs to be completed.

Project strengths:

- The project is well planned, and it is clear that the principal investigator is a leading expert in ILs. Additionally, the selected ORNL team members are all great complements to one another. The systematic approach and analysis make the project valuable to DOE. For the non-expert, the results are fairly easy to understand after some time with the material.
- There is excellent work on performing high-quality spinning and carbonized fibers. The melt-spinning approach appears to be on track as a viable option to gel-spinning fibers.
- The IL approach did allow for melt spinning of PAN. The cost benefits and carbon fiber properties are yet to be determined. The results could be a strength or a weakness.
- The project's strengths include a reduction in melt-spinning temperature.

Project weaknesses:

- The project is laser-focused on the material aspect, which is both a good and bad thing. Because of that, it is not always clear how the research is addressing the barriers seen on slide 2. For instance, it is clear that the cost is being addressed in a general way. However, the technoeconomic analysis looks at only one aspect of the cost, and it seems that maybe using the IL will actually increase the cost because of this additional component.
- The IL approach did allow for melt spinning of PAN. The cost benefits and carbon fiber properties are yet to be determined. The results could be a strength or a weakness.
- The project's weaknesses include that the team is doing economic analysis at this stage of development, when contact is being made with potential licensees.

- The project needs to have economic data.

Recommendations for additions/deletions to project scope:

- Recommendations include that the project team (1) needs a comprehensive cost model, and of particular concern is the time required to wash the fiber; and (2) needs to determine the effect of residual IL in the fiber on the mechanical properties of the carbon fiber.
- The approach of the technoeconomic analysis needs to change to focus on the cost of the PAN fibers or the carbonized fiber, using traditional PAN as a baseline. Determining the cost of the IL alone does no good in determining whether using ILs results in cost savings.
- The project team should delete the TechPAN work and concentrate on melt spinning of commercial PAN. It may be good to look at any benefits of textile PAN precursor, although melt spinning is already performed.